 Name Key

Biochemistry 5700
Fall, 2007
Exam 3

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

Have a restful and happy thanksgiving holiday!!!

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 $+ 2H^+ + 2e^- \longrightarrow \beta$-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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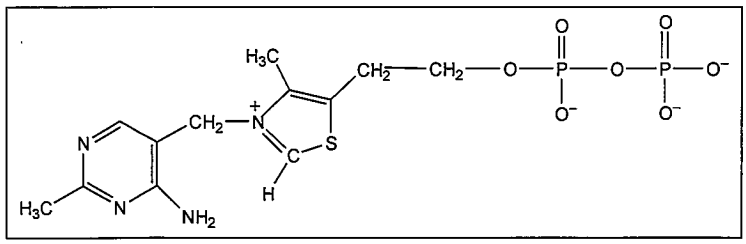

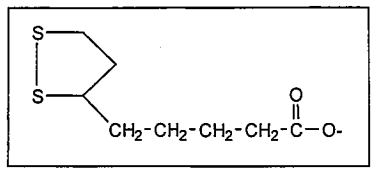

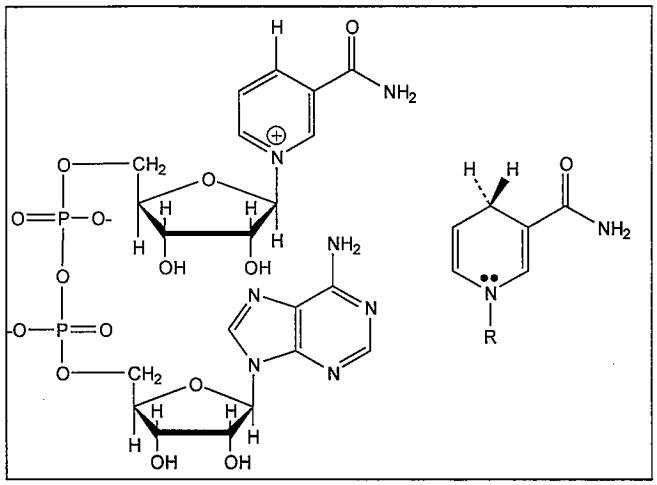

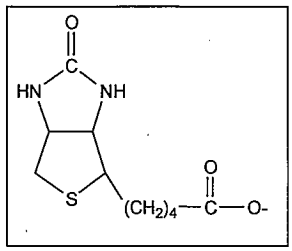

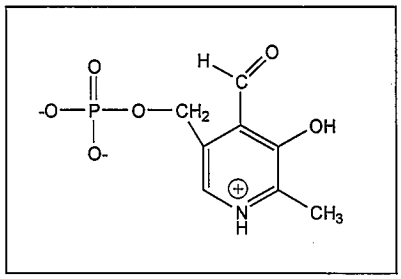

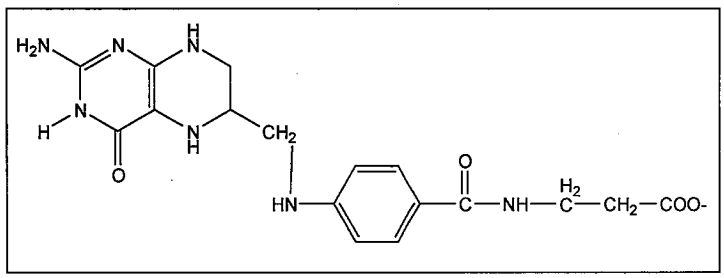

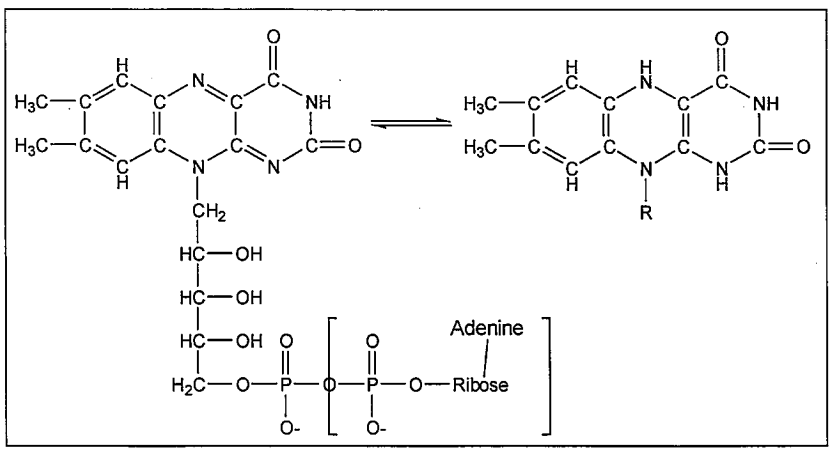

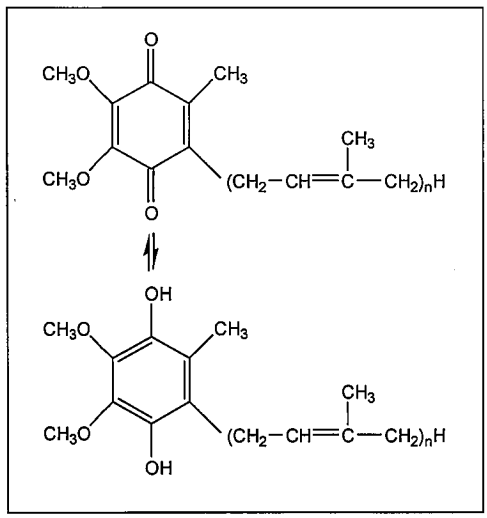

 Name Key

(1) (a) (3 points) Use information from the front page of the exam to write a balanced chemical equation for the lactate dehydrogenase reaction where pyruvate is the substrate and lactate is the product.

Pyruvate + NADH + H^+ → lactate + NAD^+

(b) (3 points) Use information from the front page of the exam to determine E°' for the reaction in (1). Is the reaction spontaneous under standard conditions? → yes

Pyruvate + ~~2H+ + 2e~~ → lactate $\quad E^{0'} = -0.185V$

NADH → NAD^+ + ~~H+ + 2e~~ $\quad E^{0'} = +0.320V$

Pyruvate + NADH + H^+ → lactate + NAD^+ $\quad E^{0'} = +0.135V$

(c) (3 points) Use the value of E°' you determined in (b) to determine ΔG°' for the reaction.

$$\Delta G^{0'} = -(2)\left(96.5 \frac{kJ}{V \cdot mol}\right)(+0.135V) = \boxed{-26.05 \frac{kJ}{mol}}$$

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(2) (5 points) Typical intracellular concentrations of ATP, ADP, and Pi in a bacterial cell are 8.0, 1.2, and 5.3 mM, repectively. What is the free energy of hydrolysis of ATP under these conditions (at 25 degrees celsius. Recall R = 8.3144 J/mol/K and ΔG'° = -30.5 kJ/mol for ATP hydrolysis to ADP and Pi.

$$\Delta G' = \Delta G^{0'} + RT \ln Q$$

$$ATP + H_2O \rightleftharpoons ADP + P_i$$

$$\Delta G' = \Delta G^{0'} + RT \ln \frac{[ADP][P_i]}{[ATP]}$$

$$\Delta G' = \frac{-30.5\,kJ}{mol} + \left(8.3144 \frac{J}{mol\,K}\right)\left(\frac{kJ}{1000\,J}\right)(298\,K) \ln \frac{(1.2 \times 10^{-3}M)(5.3 \times 10^{-3}M)}{(8.0 \times 10^{-3}M)}$$

$$\frac{-30.5\,kJ}{mol} + \frac{-17.7\,kJ}{mol} = \boxed{-48.2\,kJ/mol}$$

(3) (4 points) Match the name with the mode of growth.

Carbohydrate	Correct match letter
Light energy, acetate as carbon source	b
Energy source = hydrogen gas, CO_2 is carbon source	c
Energy and carbon source is fructose	d
Light energy, CO_2 is carbon source	a

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

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(4) 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.**

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(5) (4 points) What are the four general classes dicussed in class that all metabolic enzymes can be grouped into?

(i) group transfer
(ii) oxidation/reduction
(iii) isomerization/ elimination/ rearrangement
(iv) C-C bond forming / breaking

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(6) (8 points) Circle all of the following compounds that are correctly referred to as "high energy compounds". Then, write below EACH compound (not just the high energy ones) the specific class (family; name, such as alkyl phosphate, acyl phosphate, etc) of compound to which it belongs.

succinyl-CoA — thioester
1,3-diphosphoglycerate — acyl phosphate
2-phosphoglycerate — alkyl phosphate
3-phosphoglycerate — alkyl phosphate
glucose-1-phosphate — alkyl phosphate
phosphoenolpyruvate — enol phosphate
creatine phosphate — phosphoguanidinium
fructose-1,6-diphosphate — alkyl phosphate

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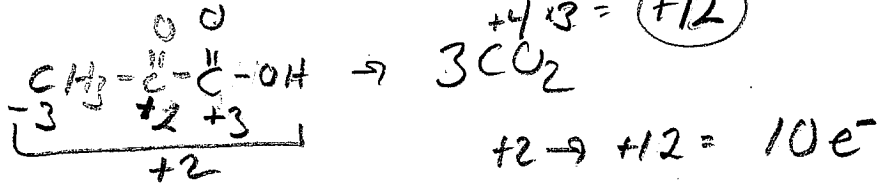
(7) (6 points) Oxidation of glucose to two pyruvate releases 4 electrons; oxidation of one pyruvate to ~~three~~ CO_2 releases 10 electrons, and the complete oxidation of glucose to CO_2 and water releases 24 electrons.



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(8) (3 points) The conversion of **2 mol** of pyruvate to **6 mol** of CO_2 via pyruvate dehydrogenase and the citric acid cycle also yields 8 mol of NADH, 2 mol of $FADH_2$ (bound to succinate dehydrogenase) , and 2 mol of GTP.

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(9) (4 points) For the pyruvate dehydrogenase complex, name the cofactor that:

(a) Accepts the acetyl group from reduced lipoamide — Coenzyme A (CoA)

(b) oxidizes $FADH_2$. — NAD+ (nicotinamide adenine dinucleotide)

(c) is the initial electron acceptor in oxidation of pyruvate. — lipoamide (lipoic acid)

(d) attacks and attaches to the central carbon in pyruvate. — thiamine pyrophosphate (TPP)

(e) oxidizes the reduced form of lipoic acid. — FAD (flavin adenine dinucleotide)

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(10) (4 points) Circle the correct term (e.g. either liver or muscle, activation or inactivation) from the underlined choices to complete the sentences.
Glucose binds an allosteric site on glycogen phosphorylase in the **liver**/**muscle** which results in **activation**/**inactivation** of the enzyme, while AMP binds an allosteric site on glycogen phosphorylase in the **liver**/**muscle** which results in **activation**/**inactivation** of the enzyme.

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(11) (5 points) Name the enzyme from the citric acid cycle that catalyzes each of the following reactions:

(a) isomerization — aconitase

(b) claisen condensation — citrate synthase

(c) oxidative decarboxylation using thiamine pyrophosphate (TPP) — α-ketoglutarate dehydrogenase

(d) oxidative decarboxylation not requiring TPP — Isocitrate dehydrogenase

(e) net substrate hydration — fumarase

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(12) (2 points) You have two unlabelled isozymes of hexokinase. Kinetic analysis reveals that the K_m for the first isozyme is 0.1 mM and the K_m for the second isozyme is 10 mM. Isozyme 1 is (circle one): hexokinase/glucokinase.

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(13) (2 points) When glucose is metabolized by the oxidative portion of the pentose phosphate pathway, C-1 of glucose would be expected to end up principally in what product?

CO_2

 Name Key

(14) (5 points) Match the correct strategy for the INITIAL STEP in getting the indicated sugars into glycolysis. Some choices may be used more than once, or not at all

Carbohydrate	Correct match letter
Stored glycogen	b
Dietary sucrose	a
Dietary fructose	c
Dietary lactose	a
Dietary galactose	d or c

Match choices:
(a) hydrolysis
(b) phosphorolysis
(c) phosphorylation from ATP
(d) nucleotide transfer/epimerization

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(15) (2 points) Name the compounds from #14 that will also require the action of a mutase to enter glycolysis.

galactose, glycogen (stored)

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(16) (5 points) What is the correct sequence of events involved in hormonal activation of glycogen breakdown in the muscle? Number the following steps in the order in which they occur (1 to 7).

Step	step
Production of cAMP	4
Conformational change in G protein	2
Activation of glycogen phosphorylase	7
Binding of epinephrine to cell receptor	1
Activation of phosphorylase kinase	6
activation of protein kinase	5
Migration of G_α to adenylyl cyclase	3

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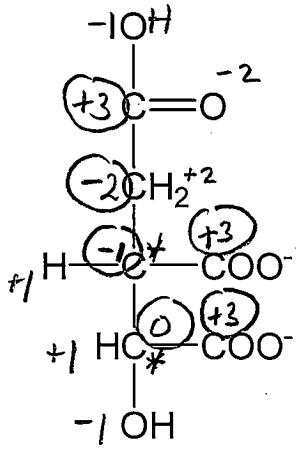
(17) (6 points) Name the following compound, then assign correct oxidation numbers to each carbon atom in the compound. Finally, mark any stereocenters with an asterisk (*)



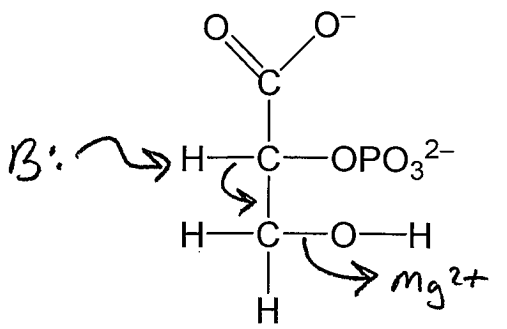
isocitrate (+1)

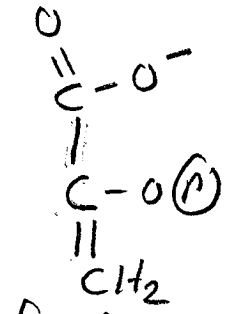
 Name Key

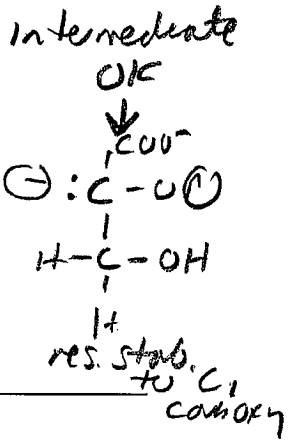
(18) (12 points) For each of the following substrates, initiate the reaction mechanism for the transformation of that substrate by adding all the necessary general acids/bases/cofactors, and show all electron pushing, for the FIRST STEP in the transformation. Then show the intermediate or product formed from that first step.

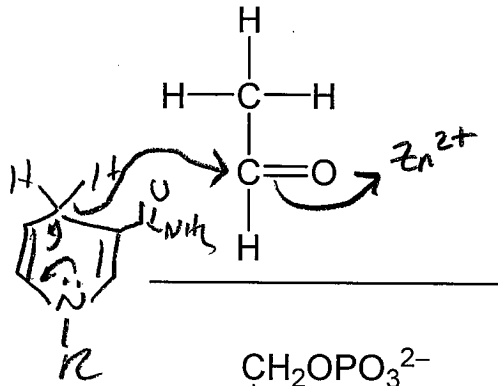
SUBSTRATE

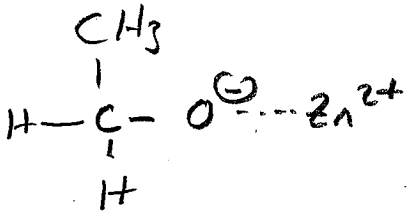
INITIAL INTERMEDIATE OR PRODUCT

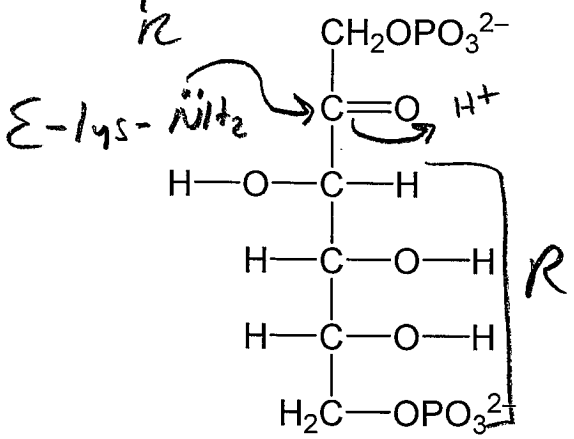


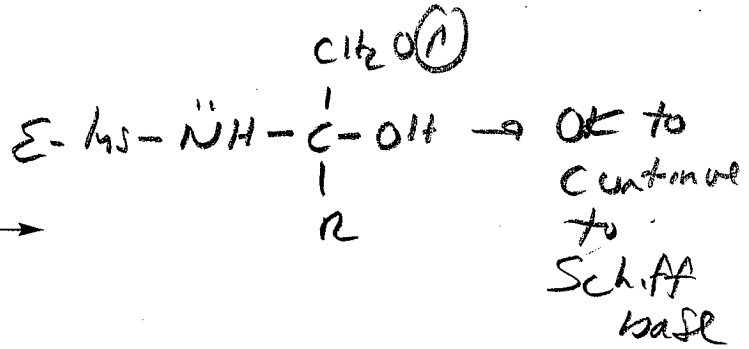


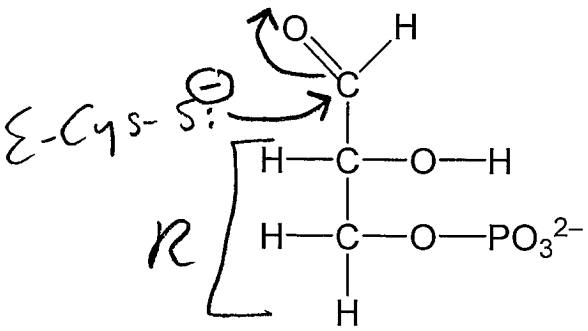


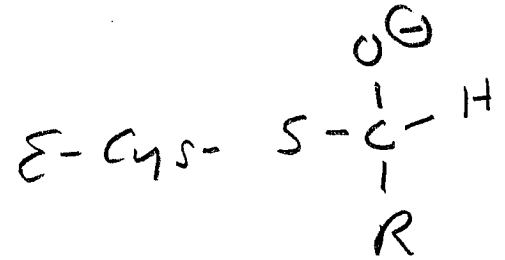












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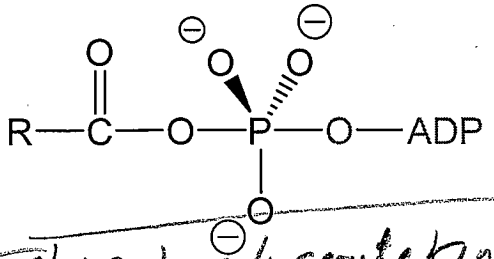
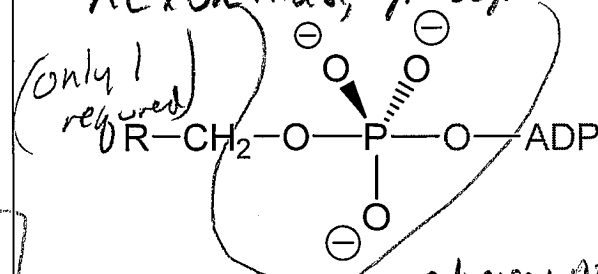
(19) (8 points) The following are pentavalent intermediates that might be formed in reactions in glycolysis. For each one, name a specific glycolytic enzyme where that intermediate would be formed, and then write the overall reaction catalyzed by the enzyme (names only in reaction, no structures).



phosphoglycerate kinase

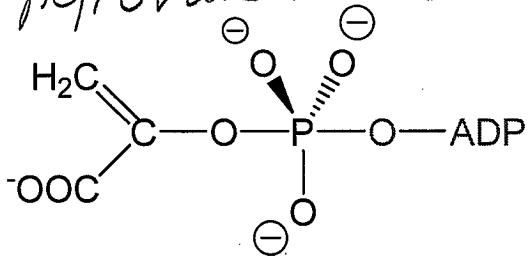
1,3-diphosphoglycerate + ADP → 3-phosphoglycerate + ATP



hexokinase, phosphofructokinase (only 1 required)

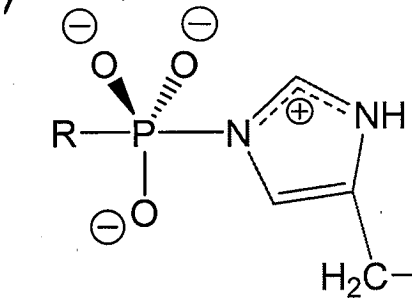
glucose + ATP ⇌ Glc-6-(P) + ADP

fructose-6-(P) + ATP → frc 1,6-di-(P) + ADP



pyruvate kinase

phosphoenolpyruvate + ADP → pyruvate + ATP



phosphoglyceromutase

3-phosphoglycerate ⇌ 2-phosphoglycerate

(20)

(a) (2 points) In a single sentence, explain the difference between a "synthase" and a "synthetase".

Synthase forms a C-C bond without using E of ATP hydrolysis; synthetase catalyzes a reaction using ATP hydrolysis

(b) (2 points) Write the balanced chemical equation for the reaction catalyzed by the citric acid cycle enzyme that is named a "synthetase".

Succinyl-CoA + GDP + P_i ⇌ succinate + CoA + GTP