Name Key

Chem 352 - Fall 2018 - Exam III

Use constants: Ideal gas law constant, $R = 0.08206$ (l•atm)/(mol•K) = 8.314 (J/(mol•K); Faraday's constant, $\mathscr{F} = 9.659 \times 10^4$ J/(V•mol); Planck's constant, $h = 6.626 \times 10^{-34}$ J•s.

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1. Describe the metabolic purpose for each of the following pathways:

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3 a. Gluconeogenesis: This is the metabolic pathway that leads to the net synthesis of glucose from pyruvate, and other glycolytic intermediates.

3 b. The citric acid cycle, when material enters the cycle as oxaloacetate: In this case, the end product of glucolysis, pyruvate is carboxylated to oxaloacetate. This increases the concentrations of all of the citric acid cycle intermediates, which can either speed up the citric acid cycle , or be used as starting material for various biosynthetic pathway.

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3 c. The lactic acid fermentation pathway: The is the pathway used by bacteria and mammalian muscles to reoxidize the NADH + H^+ that is produced in glycolysis. This is done when the electron transport chain is not an option and oxidized NAD^+ is needed to keep the glycolytic pathway active for the purpose of phosphorylating ADP to produce ATP.

3 d. Glycolysis: This is the pathway used to break the six-carbon glucose molecule down into two three-carbon pyruvate molecules, with the concomitant production of two ATP molecules. It also involves the reduction of 2 NAD^+, to 2 NADH+H^+.

3 e. The citric acid cycle, when material enters the cycle as Acetyl-CoA: This is the catabolic route into the citric acid cycle. The two carbons that enter the cycle as acetylCoA, leave as CO_2. The hydrogens that enter the cycle as either acetyl-CoA or water, leave by reducing NAD^+ to NADH + H^+

3 f. The non-oxidative phase of the pentose-phosphate pathway: The oxidative phase of the pentose-phosphate pathway starts with a six-carbon glucose-6-phosphate molecule and oxidatively decarboxylates it to produce a five carbon sugar, ribulose-5-phosphate and reduce $NADP^+$ to NADPH. If five carbon sugars are not needed, the non-oxidative phase can then be used to convert three ribulose-5-phosphate molecules back into the glycolytic intermediates, producing two fructose-6-phosphate molecules plus one glyceraldehyde-3-phosphate molecule. These can then either be broken down in glycolysis to produce ATP, or used in gluconeogenesis to synthesize more glucose-6-phosphate

2. The light reactions of photosynthesis and the electron transport chain in plants share many common features.

   a. Identify the components of each that fit the following descriptions:

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	Photosynthesis	Electron Transport Chain
The initial donor of electrons	1 H_2O	1 NADH + H^+
The final acceptor of electrons	1 $NADP^+$	1 O_2
The mobile 1-electron carrier involved in the Q cycle	1 Plastocyanin (PC)	1 Cytochrome *c* (*cyt c*)
The mobile 2-electron carrier involved in the Q cycle	1 Plastoquinone (PQ)	1 Ubiquinone (Q)
The name of the complex that is site of the Q-cycle	1 Cytochrome *bf* (*cyt bf*)	1 Complex III
Cellular location of each in eukaryotes	Chloroplast the thylakoid membrane 1	Mitochondrial inner membrane 1

Reduction half-reaction	$E°'$ (V)
Acetyl CoA + CO_2 + $H^{\oplus}$ + $2e^{\ominus}$ → Pyruvate + CoA	−0.48
Ferredoxin (spinach). Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	−0.43
2 $H^{\oplus}$ + $2e^{\ominus}$ → H_2 (at pH 7.0)	−0.42
α-Ketoglutarate + CO_2 + 2 $H^{\oplus}$ + $2e^{\ominus}$ → Isocitrate	−0.38
Lipoyl dehydrogenase (FAD) + 2 $H^{\oplus}$ + $2e^{\ominus}$ → Lipoyl dehydrogenase ($FADH_2$)	−0.34
$NADP^{\oplus}$ + $H^{\oplus}$ + $2e^{\ominus}$ → NADPH	−0.32
$NAD^{\oplus}$ + $H^{\oplus}$ + $2e^{\ominus}$ → NADH	−0.32
Ubiquinone (Q) + 2 $H^{\oplus}$ + $2e^{\ominus}$ → QH_2	0.04
Cytochrome c, Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.23
Plastocyanin, Cu^{2+} + $e^{\ominus}$ → Cu^{+}	0.37
$NO_3^{\ominus}$ + 2 $H^{\oplus}$ + $2e^{\ominus}$ → $NO_2^{\ominus}$ + H_2O	0.42
Photosystem I (P700)	0.43
Fe^{3+} + $e^{\ominus}$ → Fe^{2+}	0.77
$\frac{1}{2}O_2$ + 2 $H^{\oplus}$ + $2e^{\ominus}$ → H_2O	0.82
Photosystem II (P680)	1.1

3. Photosystem I (P700) in plants receives an electron from a plastocyanin molecule and uses light energy (photons) to give this electron enough energy to reduce a ferredoxin molecule.

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a. Write the *net reaction equation* for the reduction of one ferredoxin molecule by one plastocyanin molecule.

$E^{o'}$

$\text{Plastocyanin}_{red} \longrightarrow \text{Plastocyanin}_{ox} + e^-$ -0.37 V

4 $\text{Ferredoxin}_{ox} + e^- \longrightarrow \text{Ferredoxin}_{red}$ -0.43 V

$\text{Plastocyanin}_{red} + \text{Ferredoxin}_{ox} \longrightarrow \text{Plastocyanin}_{ox} + \text{Ferredoxin}_{red}$ $\Delta E^{o'} = -0.80$ V

b. Using the appropriate reduction potentials provided in the table above, calculate the minimum light energy required to drive this reaction under standard condition?

$\Delta G°' =$ -77.3 kJ/mol

$$\Delta G^{o'} = -n\mathcal{F}\Delta E^{o'}$$

$$= -(1)\left(9.659 \times 10^4 \frac{\text{J}}{\text{mol•V}}\right)(-0.80\text{ V})$$

$$\Delta G^{o'} = +77{,}300 \frac{\text{J}}{\text{mol}} = +77.3 \frac{\text{kJ}}{\text{mol}}$$

c. Two reduced ferredoxin molecules produced by PSI can be subsequently used to reduce an $NADP^+$ to NADPH + H^+. Write the *net reaction equation* for this reaction.

$E^{o'}$

$2\ \text{Ferredoxin}_{red} \longrightarrow 2\ \text{Ferredoxin}_{ox} + 2\ e^-$ +0.43 V

4 $NADP^+ + H^+ + 2\ e^- \longrightarrow \text{NADPH}$ -0.32 V

$2\ \text{Ferredoxin}_{red} + NADP^+ + H^+ \longrightarrow 2\ \text{Ferredoxin}_{ox} + \text{NADPH}$ $\Delta E^{o'} = -0.11$ V

d. Using the appropriate reduction potentials provided in the table above, calculate the standard free energy change for this reaction?

$\Delta G°' =$ -21.2 kJ/mol

$$\Delta G^{o'} = -n\mathcal{F}\Delta E^{o'}$$

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$$= -(2)\left(9.659 \times 10^4 \frac{\text{J}}{\text{mol•V}}\right)(0.11\text{ V})$$

$$\Delta G^{o'} = -21{,}200 \frac{\text{J}}{\text{mol}} = -21.2 \frac{\text{kJ}}{\text{mol}}$$

4. Nicotinamide adenine dinucleotide (NAD^+) is one of the coenzymes commonly used by oxidoreductases.

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a. Describe the biochemical role played by NAD^+? NAD+ is one of the redox coenzymes and is commonly used to oxidize alcohols and aldehydes in catabolic pathways. Because it has a high

4 negative reduction potential, it can store a good bit of chemical energy when in its reduced state. It is also a mobile coenzyme, so can transport this energy to the electron transport where it reduces O_2 to H_2O, and use the energy released to phosphorylate ADP to ATP

b. *Using structural formulas,* write a balanced chemical reaction equation for one example of a reaction in which NAD^+ is used as the oxidizing agent.

Enzyme Name Isocitrate dehydrogenase

Reaction Equation:

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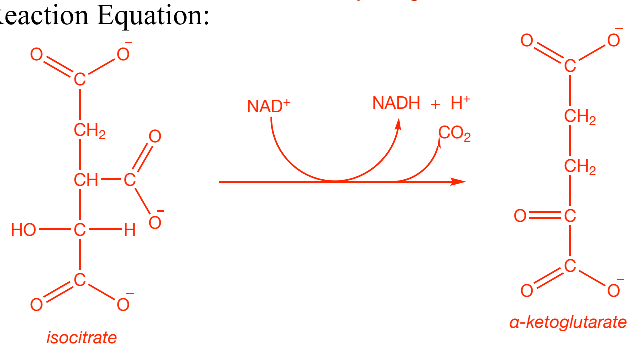

Other reactions that could be used include,

- Pyruvate dehydrogenase (connecting Glycolysis to CAC)
- α-ketoglutarate dehydrogenase (CAC)
- Malate dehydrogenase (CAC)
- Glyceraldehyde-3-phosphate dehydrogenase (Glycolysis and Gluconeogenesis)

c. What metabolic pathway does your chosen reaction belong to?

1 Citric Acid Cycle (CAC)

d. *Using structural formulas,* write a balanced chemical reaction equation for one example of a reaction in which $NADH+H^+$ is used as the reducing agent.

1 Enzyme Name Lactate dehydrogenase

Reaction Equation:

Another reaction that could be used includes,

- Alcohol dehydrogenase (Alcohol Fermentation

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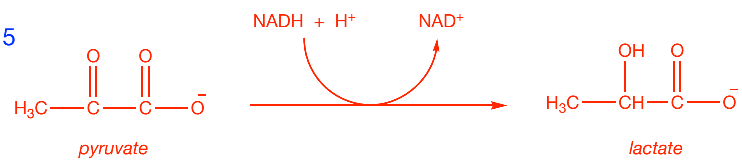

e. What metabolic pathway does your chosen example belong to?

1 Lactate fermentation pathway

5. Pyruvate represents a crossroads in metabolism where a number of metabolic pathways intersect. For example, it is the end product of the breakdown of glucose in glycolysis, it is produced in the liver from lactate in the Cori cycle, and in protein degradation, it is just one reaction away from the amino acid alanine. Pyruvate is also the starting point for a number of anabolic pathways

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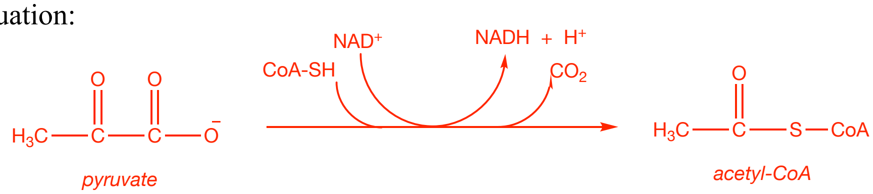
a. *Using structural formulas*, write a balanced chemical reaction equation for the first reaction leading from pyruvate to the synthesis of a fatty acid. (Fatty acids are synthesized from acetyl-CoA)

Enzyme Name Pyruvate dehydrogenase

5 Reaction Equation:



b. *Using structural formulas*, write a balanced chemical reaction equation for the first reaction leading from pyruvate to the synthesis of a glucose in the liver.
Enzyme Name Pyruvate Carboxylase
aReaction Equation:

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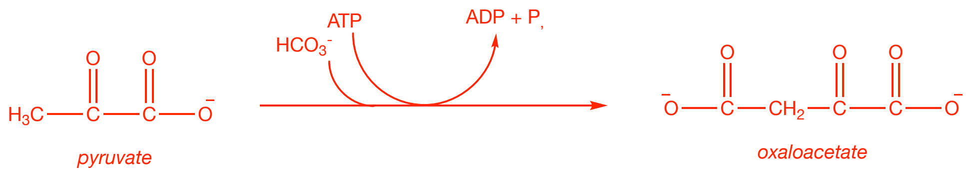

6. The pentose phosphate pathway has both oxidative and non-oxidative phases.

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a. *Using structural formulas*, sketch out the three reactions that comprise the *oxidative phase* of the pentose phosphate pathway.

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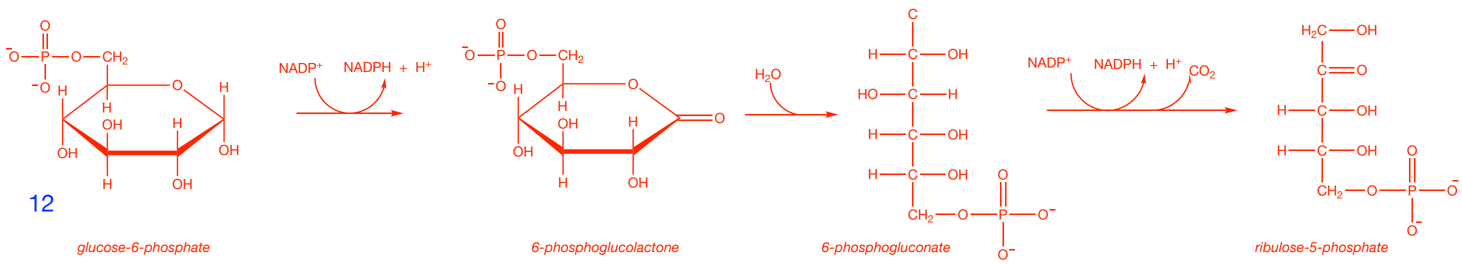

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b. Discuss the purpose of each phase and describe how they can be used in conjunction with glycolysis and gluconeogenesis to meet various needs for the cell. **The oxidative phase starts with the glycolytic intermediate, glucose-6-phosphate, and produces two products, reduced NADPH, which can be used as a reducing agent in biosynthetic pathways, and ribulose-5-phosphate, a pentose, which is needed for nucleotide biosynthesis. The non-oxidative phase can then be used to covert the ribulose-5-phosphate produced in the oxidative phase, back into glycolytic intermediates, which can then be either catabolized in glycolysis and the citric acid cycle to produce ATP, or used in gluconeogenesis to produce more glucose-6-phosphate. By combining these pathways, a cell can satisfy its needs for a number of substances, including reduced NADPH, pentoses, and/or ATP.**

7. Then enzyme phosphofructokinase 1 (PFK-1) catalyzes the first committed step in glycolysis and is therefore regulated by a number of allosteric effectors. Identify whether each of the following allosteric effectors for PFK-1 activates or inhibits PFK-1 activity. Also indicate the cellular or systemic conditions that each is signaling:

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a. Citrate: Citrate is an allosteric inhibitor of PFK-1. Elevated levels of citrate in the cytoplasm signals an abundance of citric acid cycle intermediates, and therefore no need to produce more pyruvate to elevate their levels.

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b. 2,6-bisphosphofructose 2,6-bisphosphofructose is a positive allosteric effector for PFK-1. Glucagon, the hormone that signals low blood glucose levels, also triggers the breakdown of 2,6-bisphosphofructose and removes its activating influence on PFK-1. Elevated levels of 2,6-bisphosphofructose therefore signals a lack a of need for preserving glucose for the purpose in the liver, or raising blood glucose levels.

8. Extra Credit:
   a. Ask the one question that you wanted me to ask, but I did not ask. (Up to 2 points will be awarded for an insightful, probing and well-worded question.)

   b. Answer the question you posed in part 1. (Up to 1 point will be awarded for answering your question correctly.)

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