Name Key

Chem 352 - Fall 2013
Quiz 5

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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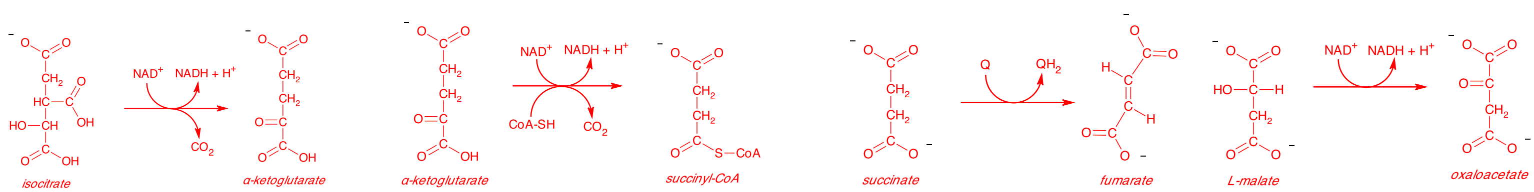
1. In its catabolic mode, the citric acid cycle is used to oxidize the equivalent of the two carbons, which enter the cycle as acetyl-CoA and are released as CO_2.

   a. Using *structural formulas* for the citric acid cycle intermediates, write a *balanced chemical equation* for *just one* of the oxidoreductase reactions in the citric acid cycle (pick one):

Four out of the eight reactions in the citric acid cycle are oxidoreductase reactions, so you have four to choose from:



isocitrate dehydrogenase | α-ketoglutarate dehydrogenase | succinate dehydrogenase | malate dehydrogenase

   b. What is the name of the enzyme that catalyzes the reaction you chose? (see above for options)

2. The oxidative stage of the pentose phosphate pathway is used to convert a glycolytic intermediate to a pentose and at the same time produce reducing agents for biosynthetic reactions.

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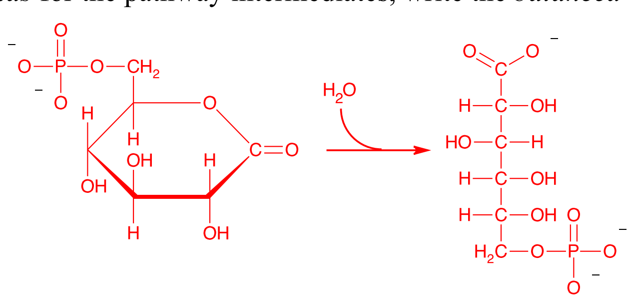
   a. Which glycolytic intermediate is the starting point for the oxidative stage of the pentose phosphate pathway? glucose 6-phosphate

   b. What is the name of the pentose produced? ribulose 5-phosphate

   c. What reducing agents are formed? NADPH + H^+

   d. Besides two oxidoreductase reactions, the oxidative stage also contains a hydrolase reaction. Using *structural formulas* for the pathway intermediates, write the *balanced chemical equation* for this reaction.



D 6-phospogluconolactone *D 6-phosphogluconate*

   e. If the pentose produced in the pentose phosphate pathway should not be required by the cell, what two glycolytic intermediates is this pentose converted to in non-oxidative stage of the pentose phosphate pathway?

      i. fructose 6-phosphate

      ii. glyceraldehyde 3-phosphate

3. In class we discuss how the electron transport chain carries out the re-oxidation of NADH + H^+ by molecular oxygen by combining lots of little steps.

   a. Write a *balanced chemical equation* for the net overall reaction that takes place in the electron transport chain, starting with one NADH + H^+.

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$$NADH + H^+ + \frac{1}{2} O_2 \rightarrow NAD^+ + H_2O$$

   b. Using the appropriate reduction potentials provided in the table below, calculate the change in the standard free energy per mole of NADH + H^+ for this overall reaction. (Show your calculations.)

Reduction half-reaction	$E°'$ (V)
Acetyl CoA + CO_2 + $H^⊕$ + $2e^⊖$ → Pyruvate + CoA	−0.48
Ferredoxin (spinach). Fe^{3+} + $e^⊖$ → Fe^{2+}	−0.43
2 $H^⊕$ + $2e^⊖$ → H_2 (at pH 7.0)	−0.42
α-Ketoglutarate + CO_2 + 2 $H^⊕$ + $2e^⊖$ → Isocitrate	−0.38
Lipoyl dehydrogenase (FAD) + 2 $H^⊕$ + $2e^⊖$ → Lipoyl dehydrogenase ($FADH_2$)	−0.34
$NADP^⊕$ + $H^⊕$ + $2e^⊖$ → NADPH	−0.32
$NAD^⊕$ + $H^⊕$ + $2e^⊖$ → NADH	−0.32
Lipoic acid + 2 $H^⊕$ + $2e^⊖$ → Dihydrolipoic acid	−0.29
Thioredoxin (oxidized) + $2H^⊕$ + $2e$ → Thioredoxin (reduced)	−0.28
Photosystem I (P700)	0.43
Fe^{3+} + $e^⊖$ → Fe^{2+}	0.77
$\frac{1}{2}O_2$ + 2 $H^⊕$ + $2e^⊖$ → H_2O	0.82
Photosystem II (P680)	1.1

$\Delta G°'$ = 220 kJ/mol

$$NADH + H^+ \rightarrow NAD^+ + 2 e^- + 2 H^+ \qquad E°' = 0.32 \text{ V}$$
$$\frac{1}{2} O_2 + 2 e^- + 2 H^+ \rightarrow H_2O \qquad E°' = 0.82 \text{ V}$$
$$NADH + H^+ + \frac{1}{2} O_2 \rightarrow NAD^+ + H_2O \qquad \Delta E°' = 1.14 \text{ V}$$

$$\Delta G°' = n \mathscr{F} \Delta E°'$$
$$= (2)\left(9.659 \text{ x } 10^4 \frac{\text{J}}{\text{V•mol}}\right)(1.14 \text{ V}) = 220{,}000 \frac{\text{J}}{\text{mol}} = 220 \frac{\text{kJ}}{\text{mol}}$$

   c. This free energy is eventually used to make ATP from ADP + P_i. Describe how this energy is first stored up for this purpose within the electron transport chain.

   The oxidation of NADH + H^+ by O_2 is coupled to the pumping of protons (H^+'s) across the inner mitochondrial membrane, creating an electrochemical gradient across the membrane.

   d. If the standard free energy change for the hydrolysis of ATP to ADP + P_i is -32 kJ/mol:

$$ATP + H_2O \rightarrow ADP + P_i \qquad \Delta G°' = -32 \text{ kJ/mol}$$

   Potentially how many moles of ATP can be produced from the re-oxidation of one mole of NADH + H^+ by molecular oxygen? (Show your calculations.)

$$\frac{220 \frac{\text{kJ}}{\text{mol}}}{32 \frac{\text{kJ}}{\text{mol}} / \text{ATP}} = 6.9 \text{ ATP's}$$

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