7.05 Spring 2020 Problem Set 10

Oxidation-reduction reactions in the Mitochondrial Respiratory Chain.

a. The NADH dehydrogenase complex of the mitochondrial respiratory chain promotes the following series of oxidation-reduction reactions, in which Fe^{3+} and Fe^{2+} represent the iron in the iron-sulfur clusters, Q is the ubiquinone, QH_2 is ubiquinol, and E is the enzyme:

   1) $NADH + H^+ + E\text{-}FMN \rightarrow NAD^+ + E\text{-}FMNH_2$
   2) $E\text{-}FMNH_2 + 2Fe^{3+} \rightarrow E\text{-}FMN + 2Fe^{2+} + 2H^+$
   3) $2Fe^{2+} + 2H^+ + Q \rightarrow 2Fe^{3+} + QH_2$

   sum: $NADH + H^+ + Q \rightarrow NAD^+ + QH_2$

   For each of these three reactions catalyzed by the NADH dehydrogenase complex, identify:
   (a) the electron donor
   (b) the electron acceptor
   (c) the oxidation half-reaction, with electrons and protons balanced if applicable
   (d) the reduction half-reaction, with electrons and protons balanced if applicable

b. All of the dehydrogenases in glycolysis and the citric acid cycle use NAD^+ (E'_0 for $NAD^+ \rightarrow NADH$ is -0.32 V) as an electron acceptor except succinate dehydrogenase, which uses covalently bound FAD (E'_0 for $FAD \rightarrow FADH_2$ in this enzyme is 0.050 V). Suggest why FAD is a more appropriate electron acceptor than NAD^+ in the dehydrogenation of succinate, based on the E'_0 values of fumarate → succinate (E'_0 = 0.031 V), NAD^+/NADH, and the succinate dehydrogenase $FAD/FADH_2$.

c. The degree of reduction of each carrier in the respiratory chain is determined by conditions in the mitochondrion. For example, when NADH and O_2 are abundant, the steady-state degree of reduction of the carriers decreases as electrons pass from the substrate to O_2. When electron transfer is blocked, the carriers before the block become more reduced, and those beyond the block become more oxidized. For each of the conditions below, predict the state of oxidation of ubiquinone and cytochrome *c:*
   (a) Abundant NADH and O_2, but potassium cyanide (Complex IV inhibitor) added
   (b) Abundant NADH, but O_2 exhausted
   (c) Abundant O_2, but NADH exhausted
   (d) Abundant NADH and O_2

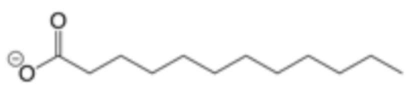
TCA cycle intermediates (adapted from a previous exam).

Arsenite is known to react with mercapto compounds, and thus it inhibits enzymatic reactions in which a thiol group is necessary.

a. Show how liver tissue could metabolize pyruvate in the presence of arsenite, plentiful supplies of ATP, and reduced coenzymes. What compound would accumulate?
b. In addition to the compound that accumulates in part (a), show how glycogen could accumulate under these conditions.

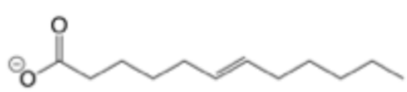
Fatty Acid Properties

Number the fatty acids below in order based on melting temperature with the lowest melting temperature fatty acid being #1. In addition, draw the fatty acid if its name is given and name the drawn fatty acid.



12:3 Δ5,8,11

20:0

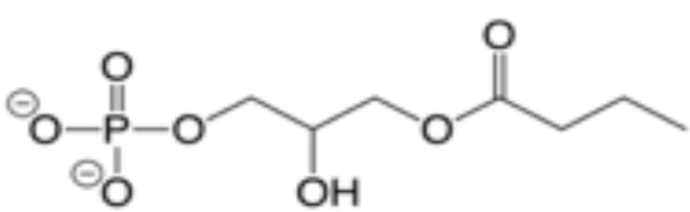


16:0

12:2 ω3,6

Fatty Acid Oxidation

a. How many NADH, FADH2, CO2, and ATP can a single molecule generate when fully oxidized. Are there any other byproducts remaining?



b. If a diet consisted only of this molecule, could the organism net produce glucose?

Introduction to photosynthesis.

a. Conceptually, oxidative phosphorylation and photophosphorylation have a lot in common. Fill in the chart below to indicate the similarities and/or differences between the two processes.

	OxPhos	**Photosynthesis light reactions**
Energy source which drives the reaction		
Compartment with low pH		
Compartment with high pH		
To create a proton gradient, both organelles use an		
Motor protein required for the generation of ATP		
High-energy molecules that are produced by the cycle		
Additional product(s)		

b. What role does water play in photosynthesis? Is it necessary?
c. What role does light play in photosynthesis? Is it necessary?
d. One product of the light reactions in photosynthesis is NADPH. What is this reduced compound used for?

Photosynthesis II (Adapted from a previous exam)
After graduation you are hired by a metabolic engineering company and are placed on a project developing fluorescent plants that emit infrared light. To accomplish this, you modify Photosystem II (PSII; which absorbs 680 nm light) such that it emits a longer wavelength.

a. In wild type plants where is PSII located?

b. Consider what effects engineering PSII to emit infrared light with have on the light reactions of photosynthesis. Will this engineering increase, decrease or have no effect on the effect of NADPH production?

You successfully engineer your plant such that you can induce all of the PSII in the mature vegetative plant to switch to a mutant form that emits infrared light. After several hours the plant appears healthy, and you find your leaves do emit infrared light. However, the next day you find your plant is dead. Further study shows that the plant dies when exposed to darkness.

c. Consider what effect engineering PSII to emit infrared light will have on the dark reactions of photosynthesis. Explain why the plant dies during periods of darkness.