Discussion Exercise 10: Biological redox reactions

Skill 1: Qualitative understanding of reduction potential

- Redox half reactions are written as an oxidized compound accepting electrons to become reduced
- If this reaction is favorable, we say that the oxidized compound has a "high reduction potential", meaning that it has a high potential to be reduced (gain electrons)
- Compounds like oxygen have a large positive reduction potential ($E_o{}' = 0.82$ V)—oxygen has a high reduction potential
- Compounds like NAD^+ have a large negative reduction potential ($E_o{}' = 0.82$ V)—NAD^+ has a low reduction potential
    - Therefore, the opposite reaction, in which NADH loses electrons is favorable
    - NADH is a powerful reducing agent and will tend to lose electrons
- Electron flow will tend to move spontaneously toward compounds that have higher reduction potential

Problem 1: The electron transport chain in a pathogenic gram-negative bacterium reveals that presence of these five electron-transport molecules. Their reduction potential are written next to them.

NAD^+ (-0.32 V); Flavoprotein b (-0.62 V); Cytochrome c (+0.22V); Ferroprotein (+ 0.85V); Flavoprotein a (+0.77V)

Predict the sequence of carriers in the electron transport chain.

Problem 2. Why is it unlikely that oxygen is the terminal electron acceptor in the bacterium from problem 1? (Refer to table 20.1 in your book.)

Skill 2: Determining the standard reduction potential of a reaction from its half reactions

- Any redox reaction can be split into two half reactions.
    - One of the half reactions is written in the standard form found on a reduction potential table, $A_{ox} + n\ e^- \rightarrow A_{red.}$
    - One of the half reactions is written in the opposite direction found on a reduction potential table, $A_{red} \rightarrow. A_{ox} + n\ e^-$. Switch the sign of the reduction potential for this half reaction.
- The reduction potential for the full reaction can be solved by Hess' law, addition of the reduction potential for the two half reactions.

Problem 3. For each of these redox reactions, write the two half reactions, then calculate the reduction potential for the overall reaction. (See Table 20.1.)

A. cytochrome c (+3) + cytochrome b (+2) → cytochrome c (+2) + cytochrome b (+3)

B. $NADH + NADP^+ \rightarrow NADPH + NAD^+$

C. α-ketoglutarate + 2 H^+ + FAD → succinate + $FADH_2$ + CO_2

Skill 3: Using standard reduction potential to answer questions concerning free energy changes

- The standard free energy of a redox reaction can be determined if the standard reduction potential is known and the number of electrons transferred is known
- $\Delta G^{o\prime} = -nF\Delta E_o{}'$ where n = # electrons, and F = 96,485 J/mol V

Problem 4: Do problem 19 from Chapter 20 in the book.

Problem 5: Nitrite is toxic to many organisms, but there are some can oxidized nitrite to nitrate and use the free energy released by the transfer of electrons to oxygen to drive ATP formation. How much energy is released when two electrons from nitrite are used to reduce oxygen to water? Use Table 20.1 and the equation below:

$$NO_3^- + 2\ H^+ + 2\ e^- \rightarrow NO_2^- + H_2O \qquad E^{o\prime} = 0.42\ V$$

Problem 6: Without using a calculator, what is the equilibrium constant for this reaction? Explain how you determined the equilibrium constant.

$$NADP^+ + NADH \rightarrow NADPH + NAD^+$$