Discussion Exercise 10: Biological redox reactions

Key

Problem 1: flavoprotein b → NAD+ →cytochrome c → flavoprotein a → ferroprotein

Problem 2. The standard reduction potential of ferroprotein is slightly larger than the standard reduction potential for oxygen, so oxygen would not spontaneously accept electrons from ferroprotein under standard conditions.

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)

Cyt c (+3) + e- → cyt c (+2) E_o' = + 0.22 V

Cyt b (+2) → cyt b (+3) + e- E_o' = - 0.07 V

For the overall reaction, E_o' = +0.15 V

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

$NADP^+ + 2e^- + H^+ \rightarrow NADPH$ E_o' = - 0.32 V

$NADH \rightarrow NAD^+ + 2\ e^- + H^+$ E_o' = + 0.32 V

For the overall reaction, E_o' = 0 V

C. α-ketoglutarate + 2 H^+ + NAD^+ → succinate + NADH + CO_2

$NAD^+ + 2e^- + 2H^+ \rightarrow NADH$ E_o' = - 0.32 V

Succinate + CO_2 → α-ketoglutarate + 2e- E_o' = + 0.67 V

For the overall reaction, E_o' = + 0.35 V

Note: This is the reaction of α-ketogluterate dehydrogenase, which is irreversible and spontaneous. α-Ketoglutarate is a strong reducing agent because its product, succinate has a very low reducing potential in this reaction.

Problem 4: See answer key in book

Problem 5:

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

$\frac{1}{2}\ O_2 + 2\ e^- + 2\ H^+ \rightarrow H_2O$ $\quad E^{o'} = 0.82$ V

So the overall process has $E^{o'} = 0.40$ V

$\Delta G^o = -nF\ E^{o'} =$ -2 (96,485 J/mol V) (0.40V) = -77.2 kJ/mol

Problem 6: The reduction potential of NAD^+ and $NADP^+$ are both -0.32 V. Therefore, the change in reduction potential for the reaction must be zero. Therefore:

$\Delta G^o = -nF\ E^{o'} =$ zero, and when the standard free energy is zero, the equilibrium constant is 1.