NAME KEY

MMBB 380 - Fall 2007
HOMEWORK #8 - Oxidation-Reduction

This homework is due 5:30 PM on Monday, Nov 12; please turn in at the 7:30 AM class, at my office (Gibb 131) or at the Review (5:30 in LSS 277). Please show your work.

(10,000 pts)

1. Malate dehydrogenase acts in the Citric Acid Cycle and can also function in Gluconeogensis. Reduction potentials for potentially useful half-reactions follow:

$OAA + 2H^+ + 2e^- \rightleftharpoons$ malate	$E°' = -0.166$ V
$NAD^+ + H^+ + 2e^- \rightleftharpoons NADH$	$E°' = -0.320$ V
$FAD + 2H^+ + 2e^- \rightleftharpoons FADH_2$	$E°' = -0.219$ V

a) Using the standard reduction potentials, *calculate* ΔE°′ and ΔG°′ for the conversion of malate to oxaloacetate (OAA) as described in class.

$NAD^+ + H^+ + 2e^- \rightleftharpoons NADH$	$E°' = -0.320$ V
malate $\rightleftharpoons OAA + 2H^+ + 2e^-$	$E°' = +0.166$ V
malate $+ NAD^+ \rightleftharpoons OAA + NADH + H^+$	$\Delta E°' = -0.154$ V

$\Delta G°' = -nF\Delta E°' = -(2)(96.485 \text{ kJ/ V mol})(-0.154 \text{ V}) = +29.72 \text{ kJ/mol}$

b) Which molecule functions as the oxidant in the forward reaction (production of OAA)?

NAD^+; The oxidant is the species that is oxidizing the other species; the oxidant picks up the electrons and becomes reduced

c) Which molecule functions as the reductant in the forward reaction? malate

The reductant is the species that reduces the other species; the reductant donates electrons in the reaction

d) Under standard conditions and *inside the mitochondrion*, would this enzyme-catalyzed reaction favor the Citric Acid Cycle or Gluconeogenesis?

Gluconeogenesis: The ΔG°′ for Citric Acid Cycle production of OAA is positive. Standard conditions favor production of malate; this occurs during use of the malate shuttle in gluconeogenesis.

(10,000 pts)

2. In aerobic organisms, Complex IV in the Electron Transport system (ETS) is responsible for passing electrons from cytochrome c to molecular oxygen. Let's imagine an anaerobic organism where complex IV donates the electrons to NO_3^- to form NO_2^- (reduction potential = 0.421 V; see Table 13-7, pg 163 of our notes).

a) Calculate the ΔE°′ and the ΔG°′ for the 2 e- reduction of NO_3^- to form NO_2^- using two reduced cytochrome c (Fe^{+2}). Show the half-reactions and the net reaction. Compare this to the ΔG°′ for the 2 e- transfer from cytochrome c to ½ O_2 determined in the extra hour.

2 Cyt c (Fe^{+2}) → 2 Cyt c (Fe^{+3}) + 2 e^-	E°′ = -0.254 V
NO_3^- + 2 H^+ + 2 e- → NO_2^- + H_2O	E°′ = +0.421 V
2 Cyt c (Fe^{+2}) + NO_3^- + 2 H^+ → 2 Cyt c (Fe^{+3}) + NO_2^- + H_2O	ΔE°′ = +0.167 V

ΔG°′ = −*nF*ΔE°′= -(2)(96.485 kJ/ V mol)(0.167 V) = -32.2 kJ/mol

For cytochrome c (Fe^{+2}) to ½ O_2, ΔG°′ = -108 kJ/mol (from lecture notes)

32.2/108 = ~29.8% of the energy available compared to molecular oxygen, O_2.

b) Complex III uses ubiquinol (UQH_2 or QH_2) to reduce cytochrome c_{ox} (Cyt c_{ox}). Calculate the ΔE°′ and the ΔG°′ for the 2 e- reduction of 2 Cyt c_{ox} by 1 ubiquinol .

Cyt c (Fe^{3+}) + e- ⇌ Cyt c (Fe^{2+})	E°′ = +0.254 V
UQ + 2 H^+ + 2 e- ⇌ UQH_2	E°′ = +0.060 V
2{Cytc (Fe^{3+}) + e- ⇌ Cytc (Fe^{2+})}	E°′ = +0.254 V
UQH_2 ⇌ UQ + 2 H^+ + 2 e-	E°′ = -0.060 V
2 Cytc (Fe^{3+}) + UQH_2 ⇌ 2 Cytc (Fe^{2+}) + UQ	ΔE°′ = +0.194 V

ΔG°′ = -nFΔE°′ = -2 (96.485kJ/V mol)(0.194 V) = -37.4 kJ/mol

c) If it costs 23 kJ of energy for every mole of H^+ pumped to the intermembrane space, how many protons could be pumped by complex 2 when succinate DH uses succinate to reduce ubiquinone (succinate + UQ ⇌ fumarate + UQH_2 ΔE°′ = +0.029 V; assume this a 2 electron reaction as shown here and that we are operating under standard conditions). Calculate the ΔG°′ for this redox reaction. Does it make sense from this comparison that Complex II doesn't pump any protons while Complex III does pump protons? (if it doesn't make sense there can always be another explanation)

The ΔG°′ for the net redox reaction mediated by Complex II in the forward direction is -5.6 kJ/mol. This is much less than the 23 kJ needed to pump a mole of H^+ across the membrane.

We don't know the cellular conditions, but it makes sense that Complex II does not pump protons while Complex III does pump protons. However, under standard conditions, there is not enough energy from 2 e- for Complex III to get 4 protons across the membrane. Cellular conditions must be more favorable.