Chem 454-Only 3 will be graded
Problems 2-SHOW ALL WORK
Due next Tuesday (15 pts)

NAME KEY

1. Below is a diagram of the inner compartment of a mitochondrion. The pH inside is 8 and outside is 5. The Transmembrane voltage, $\Delta\Psi$ is –0.06 V inside negative. SHOW ALL WORK

a. What is the $\Delta G'$ for translocation of one mole of protons from inside to outside?

$2.3RT(pH_{mat} - pH_{cyto}) + F\Delta\Psi$

$2.3 \cdot 1.98 \cdot 298 \, (3) + 23000 \cdot 0.060$

$= 4071 + 1380 = {}^{+}5450$ cal/mol

+5.4 kcal/mol

b. What is the $\Delta G'$ for transport of one mole of protons from outside to inside?

–5.4 kcal/mol

c. What is the minimum number of protons (whole number) flowing in which could drive synthesis of 1 ATP, under these conditions?

2 (since you need +7.3 kcal/mol)

d. Some Uncoupler Protein 1 is added to the mixture. The pH inside becomes 7 and outside is 6.5. The $\Delta\Psi$ = –0.02 V, inside negative. How many protons would now be required to synthesize 1 mole of ATP.

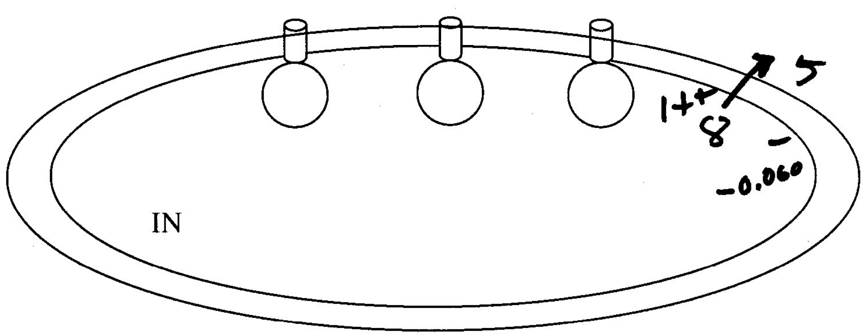
$2.3 \cdot 1.98 \cdot 298 (0.5) + 23{,}000 \times 0.02$

$680 + 460 = 1.14$ kcal/mol out → in

at least 7 H^+/ATP

e. (circle) Oxygen uptake would be expected to (Increase, Decrease) and fatty acid oxidation would be expected to (Increase, Decrease) under the conditions in (d).

(due to H^+ leak)



OUT

2. In muscle cells pyruvate is reduced to lactate under anaerobic condition (below). In the liver lactate is reoxidized to pyruvate and fed into gluconeogenesis. What is the minimum (i. e. $\Delta G' \leq 0$) NAD+/NADH ratio necessary to get net oxidation of lactate to pyruvate assuming both lactate and pyruvate are present at the same concentration (1:1)? SHOW WORK

oxidation

Pyruvate + NADH $\longrightarrow$ NAD+ + lactate

= - 2·23000 (-.19 - -.32) = -6.0 kcal/mol

		#electrons	Std. Red. Potential $E^{o\prime}$
Pyruvate/lactate	acc	2	- 0.19 V
NAD+/NADH	donor	2	- 0.32 V

$\Delta G^{o\prime} = -nF\,\Delta E^{o\prime}$ T = 310 K

$\Delta G' = \Delta G^{o\prime} + RT \ln \frac{\text{products}}{\text{reactants}}$

0 = -6,000 cal + 1.98·298 ln P/R

+6000 = 590 · ln P/R

10.2 = ln P/R

$e^{10.2}$ = P/R ≈ 26000 / 1 is NAD+ / NADH

3. A mitochondrial suspension treated with the H+ carrier FCCP has a ΔpH of 0 but still has a ΔΨ of 0.150 V (inside negative). What is the ΔG for transport of a mole of H+ into the matrix? Energetically, how many moles H+ would it take to synthesize a mole of ATP from ADP and Pi under standard conditions under these circumstances.

ΔG = 0 + 23,000 x 0.15 = -3.45 kcal/mol

In = -3.45 (3 H+ to get more than -7.3)

4. Cytochrome c passes it's single electron through complex IV to oxygen. What is the $\Delta G^{o\prime}$ for this process if 4 cytochrome c's pass on their electrons to O_2 bound to complex IV? What would be the K_{eq} for this process? What is the maximum number of ATPs which could be synthesized in this 4 electron process?

-4 * 23,000 x (0.82 - 0.22) = -55.2 kcal/mol

= 7 ATP

5. The $\Delta G^{o\prime}$ for hydrolysis of ATP is -7.3 kcal/mol.

a. Calculate the equilibrium constant for this reaction.

ΔG° = -RT ln Keq

-7300 = - 1.98·298 ln Keq

Keq = $e^{12.4}$ ≈ 240,000 / 1

b. A hypothetical reaction A $\leftrightarrow$ B has a $K_{eq'}$ of 10^{-5}. Could ATP hydrolysis under standard conditions drive this reaction? **SHOW WHY OR WHY NOT**

Yes

10^{-5} x 240,000 = 2.4

c. If the [ATP]/[ADP] *[Pi] concentration ratio were 2.0 X 10^{-2}, would the feasibility of the coupled reaction change? SHOW WHY OR WHY NOT.

ΔG° = -1.98*298 ln 1/10^5 = 6.8 kcal mol

-7300 + 1.98·298 ln 50

-7300 + 2300 = -5000 kcal/mol = -5.0 kcal/mol

ATP ⇌ ADP + Pi   1 / 2.0 x 10^{-2} = K = 50

ADP + Pi ⇌ ATP = 2.0 x 10^{-2} = K

KJd

6. A simple pathway has two steps: A $\leftrightarrow$ B $\leftrightarrow$ C

$\Delta G^{o'}$ for A $\leftrightarrow$ B = +11.4 kJ/mol, and K_{eq} is 10^{-2}
$\Delta G^{o'}$ for B $\leftrightarrow$ C = -22.8 kJ/mol, and K_{eq} is 10^{4}

a. What is the standard free energy change for conversion of A to C? __-11.4__ kJ/mol

b. Write an equation specifying the free energy change (ΔG) of the first reaction from A to B, taking into account concentrations of reactant and product: $\Delta G = -11.4$ *

c. At equilibrium what are the concentration ratios B/A, C/B, and C/A? (Hint: Base your calculation on the equilibrium constants.)
B/A = $\frac{1}{100}$ C/B = $\frac{10,000}{1}$ C/A = _____ $10^4 \times 10^{-2} = 10^2 = \frac{100}{1}$

d. If you start with 1 M each of A, B, and C, what will be the concentration of each of these compounds at equilibrium? (Hint: The total concentration of A + B + C = 3 M.)
A = __0.030__ M B = __0.000030__ M C = __2.97__ M

If [A] = x
[C] = 10,000 B
[B] = 0.01x [C] = 100x
So 3M = A + B + C = x + 0.01x + 10^2x

7. Write a sequence of <u>known</u> enzymatic reactions that will lead to a *net* synthesis of alpha-ketoglutarate from pyruvate without the <u>net</u> utilization of other TCA cycle intermediates.

pyruvate → AcCoA
Pyr carboxylase → CO_2 → OAA +

TCA

↓

αKG – <u>all</u> carbons from pyruvate – <u>net</u> increase due to OAA.