Name: SID:
Discussion Section:

Exam #2

Biophysical Chemistry

Chemistry 130A

Spring 2001

Justify all your assumptions!

Show <u>all</u> your calculations!

Make sure all your conclusions are physically reasonable.

Keep track of units and significant digits!

Underline or Box all your final answers!

Exams in pencil won't be regraded.

Keep your answers short!

Problem	*TA*	*Score*
1	J	+5/15
2		13
3		13
4		15
BONUS		0
Total		46

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Information Page

R= 8.3145 J/(K mol) = 0.08206 L atm / (K mol)

F=Faraday's constant= 9.6485 x 10^4 C/mol

$$\log(\gamma) = -0.509\, Z_i^2 \sqrt{\mu}$$

Oxidant/Reductant	Electrode Reaction	Reduction Potentials	
		ε° (V) Chemist's standard state	$\varepsilon^{\circ\prime}$ (V) Biochemist's standard state
$NAD^+/NADH$	$NAD^+ + H^+ + 2e^- \rightarrow NADH$	-0.105	-0.320
$H^+/H_2/Pt$	$2 H^+ + 2 e^- \rightarrow H_2(g)$	0.0	-0.421
Ag^+/Ag	$Ag^+ + e^- \rightarrow Ag(s)$	0.799	
Fe^{2+}/Fe	$Fe^{2+} + 2 e^- \rightarrow Fe(s)$	-0.4402	
O_2/H_2O	$\frac{1}{2} O_2 + 2 H^+ + 2e^- \rightarrow H_2O$	1.23	0.82
$FAD/FADH_2$	$FAD + 2H^+ + 2e^- \rightarrow FADH_2$		-0.219

Reaction	$\Delta G^{\circ\prime}$ kJ/mol
D-Glucose -6-Phosphate $\rightarrow$ D-Fructose-6-Phosphate	1.7
Pyruvate + NADH + H^+ $\rightarrow$ Lactate + NAD^+	-25.1
ATP + H_2O $\rightarrow$ ADP + Phosphate	-31.0
2-Phosphoenolpyruvate + ADP $\rightarrow$ Pyruvate + ATP	-31.4

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1. (15 pts) The following problems involve thinking about entropy and free energy.

a) Let the amounts of gases in two containers be n_A and n_B; both are at pressure, p, and temperature T. The chemical potential of gas A is μ_A and that of B is μ_B.

+2/5

Write down the total free energy of this system in terms of the chemical potentials. Write down the chemical potentials in terms of the standard chemical potentials and the pressures. Remember to check your units!

+1

$\mu_{TOTAL} = \mu_A + \mu_B$

$G = n_A \mu_A + n_B \mu_B$

+1

$\mu_A = \mu_A^\circ + RT \ln\left(\frac{P_f}{P_i}\right) \rightarrow \left(\frac{P_A}{1atm}\right)$

$\mu_B = \mu_B^\circ + RT \ln(\quad) \rightarrow \left(\frac{P_B}{1atm}\right)$

P

Imagine now that the partition between the two containers is removed. Write down the equation for the new total free energy.

$\Delta G = 0$ (equilibrium)

G_{MIXED}: same as a) except put P_A^* and P_B^* in place of $P_A + P_B$

+0/2

Write down the equation for ΔG_{mixing} for this process.

$\Delta G_{mixing} = \Delta G_{mixing} + RT \ln\left(\frac{P_f}{P}\right)$ → pressure of gases in final state

+0/2

ΔG_{mixing}: $G_{MIXED} - G_{UNMIXED}$: $\left[n_A(\mu_A^\circ + RT\ln(P)) + n_B(\mu_B^\circ + RT\ln(P))\right] - \left[n_A(\mu_A^\circ + RT\ln(P_A^*)) + n_B(\mu_B^\circ + RT\ln(P_B^*))\right]$

Write the equation in terms of mole fractions and determine the sign of ΔG_{mixing}.

$\Delta G = \Delta G^\circ_{mixing} + RT \ln\left(\frac{n_A + n_b}{(n_a)(n_b)}\right)$

ΔG_{mixing} is negative +1

$\frac{n_A}{n_{TOT}} : \frac{P_A^*}{P_{TOT}}$

+1/2

Write the equation for ΔS_{mixing} for the same system and what is the sign?

ΔS_{mixing} is positive +1

$\Delta S_{mixing} : -\left(\frac{\partial G}{\partial T}\right)_P$

$= -R \ln\left[\left(\frac{n_A}{n}\right)^{n_A}\left(\frac{n_B}{n}\right)^{n_B}\right]$

$\Delta S_{mixing} = \Delta G_{mixing} - \Delta H_{mixing}$ → should be 0 for an ideal gas

+2/4

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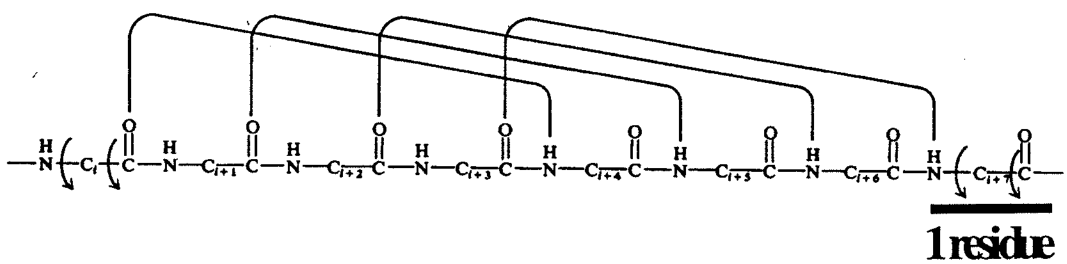
2. (15 pts) It is well known that polypeptides can adopt an α-helical conformation in solution. It is known that small changes in temperature can cause this structure to unfold in some cases. Of interest to the structural biologist is what proportion of chains in solutions are helical and which are "denatured (coiled)." Each polypeptide has only two states: completely helical or completely denatured.

a) In forming an α-helix, n-residues long the carboxy-group of one residue forms a hydrogen bond with the amino-residue 4 residues up-stream of it.

10



The free energy for converting a given residue in the helix from its free to its hydrogen bonded state is ΔG_h. This free energy is composed of the enthalpy of forming a hydrogen bond (per residue) and the change in (conformational) entropy that occurs when the bond is formed. **What is the expression for the total free energy change for converting a "denatured" polypeptide of length n to a helical polypeptide in terms of ΔH_h and ΔS_h?** (***Hint:*** Remember to consider the end-effects-- four amino groups on the left are unbonded an the terminal residues of each chain are never conformationally restricted.)

4

$\Delta G = n_{H\,bonds}(\Delta H_h) - T\Delta S_h(n_{H\,bonds})$

$n_{H\,bonds} = n - 4$

~~$\Delta H_h = \Delta G_h + T\Delta S_h$~~

~~$\Delta G = (n-4)(\Delta G_h - T\Delta S_h) - (n-4)(T\Delta S_h)$~~

~~$= (n-4)[\Delta G_h - 2T\Delta S_h]$~~

$\Delta G = (n-4)[\Delta H_h - T\Delta S_h]$

$= (n-4)\Delta H_h - T\Delta S_h(n-2)$ 4 → ΔS is neg. b/c the middle residues become more ordered

↳ all residues in middle

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b) A researcher working on a particular helix-coil transition measures the following data.

6

T(K)	324.4	326.1	327.5	329.0	330.7	332.0	333.8
Keq	0.041	0.12	0.27	0.68	1.9	5.0	21

Calculate ΔG° for this transition at 54.5 C. Estimate a value ΔH for the transition at this temperature.

$\frac{273}{327.5}$

$$\Delta G^{\circ} = -RT\ln(K_{eq})$$

$$= -8.3145 \frac{J}{K\cdot mol} \cdot (327.5K) \ln(0.27)$$

$$= 3.565 \frac{kJ}{mol}$$

✓

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H^{\circ}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \rightarrow \text{from } -RT\ln(K) = \Delta H - T\Delta S$$

assuming ΔH doesn't change from 327.5 to 329 K

$$\ln\left(\frac{0.68}{0.27}\right) = \frac{-\Delta H}{8.3145 \frac{J}{Kmol}}\left(\frac{1}{329K} - \frac{1}{327.5K}\right)$$

$$\Delta H = 551.7 \frac{kJ}{mol}$$

✓

How would you then calculate ΔS?

3

Create a Van' Hoff plot with " $\ln(K)$ vs. $\frac{1}{T}$ "

and since $\ln(K) = \frac{\Delta H}{RT} - \frac{\Delta S_{TOT}}{R}$, $\left(\frac{\Delta S_{TOT}}{R}\right)$ is the y-intercept.

Divide by $-\frac{1}{R}$ and obtain ΔS_{TOT}.

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3. **(15 pts)** Cells need to maintain a difference (gradient) in chemical concentrations across their membrane. To do this they use a number of different mechanisms including simple pores and specific chemical transport proteins.

Imagine a particular (nonionic) species maintains a concentration of c1 outside the cell and a concentration of c2 inside the cell.

What is the expression for the free energy change for transporting this species from the outside to the inside of the cell?

$\Delta G_A = \Delta G^\circ_{A^\circ} + RT\ln\left(\frac{a_A}{a_{A^\circ}}\right)$ → a_A: activity of state inside cell; a_{A°: activity of state outside cell

+6

$\gamma c_1 = a_1$ ∴ if we assume ideality (dilute solution), $c_1 = a_1$ and $\gamma = 1$. ΔG_A then equals $\Delta G_{A^\circ} + RT\ln\left(\frac{c_2}{c_1}\right)$

It is found for this species that the concentration outside the cell in 1 μM and the concentration inside the cell 1 mM. Is this process spontaneous? (Explain based on the equation and common sense.)

$\Delta G_A = \Delta G_{A^\circ} + RT\ln\left(\frac{a_A}{a_{A^\circ}}\right)$; if $a_A \approx 1\,mM$ and $a_{A^\circ} \approx 1\,\mu M$, the "$\ln\left(\frac{a_A}{a_{A^\circ}}\right)$" will be positive and unless ΔG_{A° is very negative, ΔG will be positive & nonspontaneous. This makes sense because the concentration gradient is toward the outside (flowing from higher to lower concentration regions) Thus the process won't occur.

+5

What two things would we have to consider if the species were ionic in calculating the free energy?

Ionic species have activity coefficients due to solvation shells in water that reduces their effective concentrations. Thus, their activities will be less than the concentrations c_1 & c_2 (considerably less if the species have ±2 or ±3 charges).

+2

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4. (15 pts) At the core of the electron transport chain that drives respiration is the electron transfer potential of NADH or $FADH_2$ relative to that of oxygen.

(a) What is the difference between the biochemist's and chemist's standard state? Write down the overall reaction for the reduction of oxygen by NADH. Calculate the standard free energy of this reaction? Calculate the equilibrium constant? (Use the biochemist's standard state for calculations!)

The biochemist's standard state operates at 7 pH, which is more reasonable for biological systems. Chemists use pH=0, where [H+] = 1 Molar.

15

$$NADH + \frac{1}{2}O_2 + H^+ \longrightarrow NAD^+ + H_2O$$

Biochem standard state

Half-cell rxns: $NADH \longrightarrow NAD^+ + 2e^- + H^+$ $\quad \mathcal{E}^\circ = 0.320\ V$

$2e^- + 2H^+ + \frac{1}{2}O_2 \longrightarrow H_2O$ $\quad \mathcal{E}^\circ = 0.820\ V$

$\mathcal{E}^\circ_{TOT} = 1.140\ V$

$$\Delta G^\circ = -nF\mathcal{E}^\circ = -(2\ mol\ e^-)(96.485\ \frac{kJ}{mole^-})(1.140\ V)$$

$$= 219.99\ \frac{kJ}{mol} \rightarrow 220\ \frac{kJ}{mol}$$

$96485 \frac{C}{mol}$ $\quad \frac{J}{C}$

$$\Delta G^\circ = -RT\ln(K)$$

$$220000\ \frac{J}{mol} = \left(-8.3145\ \frac{J}{K \cdot mol}\right)(298K)\ln(K)$$

(298K ↓ Standard T)

$$K = 3.62 \times 10^{38}$$

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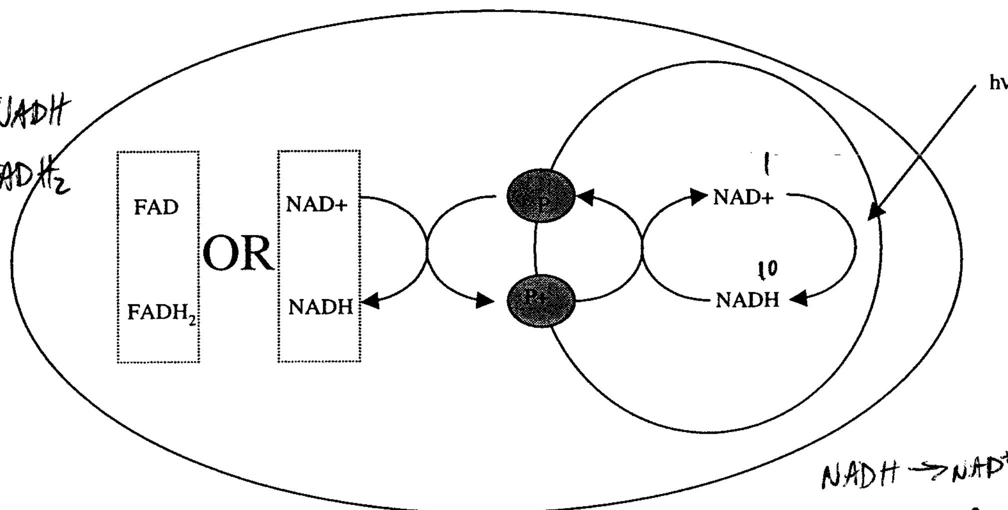
Bonus problem: 10 pts

Imagine the following cell in which NADH is generated by a photosynthetic process in a small organelle inside a cell. In turn, the NADH is used to reduce a protein in the organelle membrane and then this protein supposedly reduces either NAD^+ or FAD^+ in the cytoplasm. Imagine that this cell is illuminated such that the $NADH/NAD^+$ ratio in the organelle is maintained at 10:1. With all else at equilibrium (and at 37 °C) what ratio of $NADH/NAD^+$ can be maintained in the cytoplasm? What ratio of $FADH_2/FAD$ can be maintained in the cytoplasm? Show all how all half reactions contribute.

$NAD^+ + 2e^- + H^+ \rightarrow NADH$

$FAD + 2e^- + 2H^+ \rightarrow FADH_2$



$NADH \rightarrow NAD^+ + H^+ + 2e^-$

$\Delta G^\circ = -nFE^\circ$

$= -(2 \text{ mole}^-)(96485 \frac{J}{mol})(-.320V)$

$= -61.75 \frac{kJ}{mol}$

$\Delta G = \Delta G^\circ + RT\ln(Q)$

$= -61.75 \frac{kJ}{mol} + 8.3145 \frac{J}{K\,mol} \cdot 310K(\ln(\frac{1}{10}))$

$= -61.76 \frac{kJ}{mol}$

$-61.76 \frac{kJ}{mol} = \Delta G^\circ_{NADH} + RT\ln(Q) \rightarrow \frac{[NADH]}{[NAD^+]} = $ for NADH

$Q = .996$

$-61.76 \frac{kJ}{mol} = \Delta G^\circ_{FADH_2} + RT\ln(Q) \rightarrow \frac{[FADH_2]}{[FAD^+]}$

$-61.76 \frac{kJ}{mol} = -42.26 \frac{kJ}{mol} + RT\ln Q$

$Q = 5.18 \times 10^{-4}$ for $FADH_2$

$\Delta G^\circ_{FADH_2} = -nFE^\circ$ (0.219 V)

$= (-2 \text{ mole}^-)(96485 \frac{J}{mol})(-.219V)$

$= -42.26 \frac{kJ}{mol}$