NAME:

Chemistry 130A, Section 2, Prof. Groves

FINAL EXAM Dec. 19, 2001

8 problems: 100 points
Extra Credit: 10 points

Please:
Write in pen
Do not use whiteout
Circle your answer clearly

Information:
Gas constant R = 8.3145 J K^{-1} mol^{-1} = 0.08205 L atm K^{-1} mol^{-1}
Faraday's constant F = 9.6485 x 10^4 C mol^{-1}
Conversion L atm = 101.3 J
55.6 moles of water in 1 liter

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1. Basic principles and definitions.

   a. (4 pts) Which of the following are state variables:

Entropy	state variable	/	not a state variable
Work	state variable	/	not a state variable
Gibbs free energy	state variable	/	not a state variable
Electrical potential	state variable	/	not a state variable

   b. (4pts) For each of the following closed systems, mark which conditions are true, which are not necessarily true, and which cannot be true.

      i) Solid sucrose in the process of crystallizing from an aqueous sucrose solution:

      μ[sucrose(s)] > μ[sucrose(aq)] true / not necessarily true / cannot be true

      ii) A freshwater iceberg melting in the ocean:

      $\mu[H_2O(ice)] = \mu[H_2O(ocean)]$ true / not necessarily true / cannot be true

      iii) An equilibrium mixture of a peptide that exists in two different configurations, state1 and state2: State 1 → State 2 kinetic rate constant, $k_1 = 100\ s^{-1}$
      State 2 → State 1 kinetic rate constant, $k_{-1} = 10\ s^{-1}$

      μ[state1] = μ[state2] true / not necessarily true / cannot be true

      [state1] = 0.1 x [state2] true / not necessarily true / cannot be true

   c. (4 pts) For each of the following processes, state whether each of the requested quantitites is positive (+), negative (-), zero (0), or undetermined (U).

      i) Spontaneous folding of a protein in an adiabatic container

      $\Delta T =$ $\Delta G =$

      ii) Osmotic swelling of a red blood cell in a large bath of distilled water (37 °C, 1atm); take the red blood cell as the system. Assume the cell does not rupture.

      w = Δmass =

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2. (8 pts) Answer the following questions true or false. If false, explain why it is false.

   a. For the reaction A + B → C + D + E, one does not need to consider the products (C, D, and E) in the rate law.

   b. The kinetic order of a reaction cannot be deduced from the balanced reaction equation.

   c. Reaction orders may change over the course of a reaction.

   d. Since the rate of a zero-order reaction equals the rate constant, the rate cannot be increased or decreased.

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3. The isomerization of cis-stillbene to trans-stillbene is catalyzed by the addition of iodine, I_2:

   cis + I_2 → trans + I_2 rate constant: k

   Experimental data:

Rate d[trans]/dt	$[I_2]$	[cis]
5.59×10^{-3}	0.05 M	0.05 M
1.11×10^{-2}	0.05 M	0.10 M
4.74×10^{-2}	0.90 M	0.10 M

   (10 pts) By analyzing the above data, determine the differential rate law for this reaction in terms of [cis] and $[I_2]$ and find k.

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4. Oxides of sulfur are important in pollution.

Compound	ΔH_f^0 (kJ/mol)	ΔS_f^0 (J/ K mol)
O_2 (g)	0	205.1
H_2O (g)	-241.8	188.7
SO_2 (g)	-296.8	248.2
SO_3 (g)	-395.7	256.8
H_2SO_4 (g)	-814.0	156.9

The oxidation of SO_2 in air can occur: $1/2\ O_2 + SO_2 \leftrightarrow SO_3$

a. (10 pts) Find the equilibrium ratio of SO_3 to SO_2 in air at 25 °C. The partial pressure of O_2 in air is 0.21 atm and you may ignore involvement of H_2SO_4 for this part.

b. (10 pts) In general, the atmosphere contains an excess amount of H_2O which can react with SO_3 as follows: $H_2O + SO_3 \leftrightarrow H_2SO_4$

What form of sulfur do you expect to be the dominant form in the atmosphere? Briefly Explain your conclusion.

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5. (20 pts) Some bacteria cells create a pH gradient and voltage across the cell membrane using light to pump protons from inside the cell to the outside. This pH gradient is then used to synthesize ATP. Assume 2 protons are transported back into the cell to synthesize one ATP molecule.

   The reaction is: $ADP + HPO_4^{2-} \leftrightarrow ATP + H_2O$ $\Delta G^0 = 31$ kJ/mol
   In the cell: [ADP] = 100 μm [ATP] = $[HPO_4^{2-}]$ = 1 mM
   Voltage across cell membrane = 100 mV with inside negative relative to outside

   Assuming that all of the energy of the protons can be utilized to synthesize the ATP, what pH difference between inside and outside is needed for this reaction to occur spontaneously?

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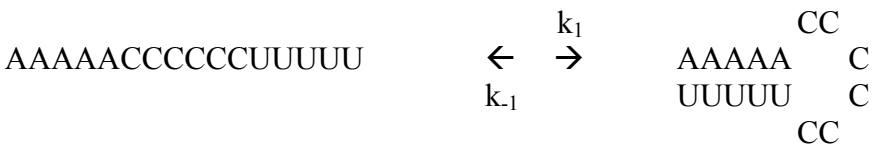
6. A single stranded oligonucleotide that has complementary ends can form a base-paired loop. For the oligonucleotide $A_5C_6U_5$:



(10 pts) At 25°C, you measure the forward rate constant $k_1 = 2 \times 10^3\ s^{-1}$. You also measure the equilibrium concentrations of the loop, $[Loop]_{eq} = 0.42$ mM, and single strand, $[SS]_{eq} = 0.58$ mM. What is the rate constant for Loop → SS, k_{-1}?

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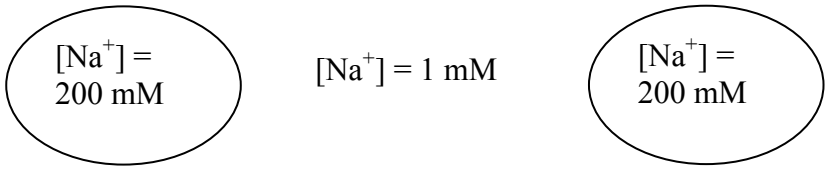
7. Consider two spherical membranes vesicles(10 μm in diameter) initially enclose a solution of 200 mM Na^+. The membranes contain pores and are leaking Na^+ to the outside environment, which is 1mM in Na^+.



Membrane 1 Membrane 2

a. (5 pts) You study two different membrane compositions, each with identical pores, and find that membrane 2 is leaking Na^+ more slowly than membrane 1. Can you deduce anything about the charge densities of the two membranes from this information? If so, what?

b. (5 pts) Which of the membranes vesicles will have a higher Na^+ concentration inside at equilibrium? Assume the pores in these membranes are not ion selective and ignore small deviations resulting from counterions to the membrane charges.

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8. A spherical protein, P, of diameter, R, dimerizes (P + P → PP). Assume the proteins rearrange upon dimerization so that the dimer is also spherical with volume equal to twice the volume of the original protein. Recall that volume = $4/3\ \pi\ r^3$; and R = 2r.

   a. (5 pts) What will be the percent increase or decrease in the diffusion coefficient?

   b. (5 pts) What will be the percent increase or decrease in the sedimentation coefficient?

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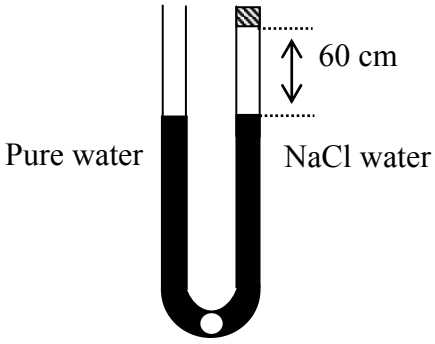
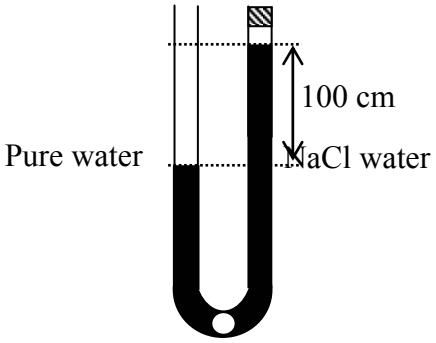
Extra Credit

Consider the following experiment:

Initial state



Final state



Data: Initial pressure both outside and inside the tube is 1 atm. T = 298 K. The tube is sealed on the right side, but is open on the left. The semipermeable barrier at the bottom is fixed in place and allows water, but not ions to pass. A ΔP of 1 atm can raise a column of water 1 m.

(5pts) What is the concentration of the salt water in the final state (right side)?

(5 pts) What will be the equilibrium configuration of the system if it is moved from 1 atm ambient pressure to high vacuum at T = 100 K?