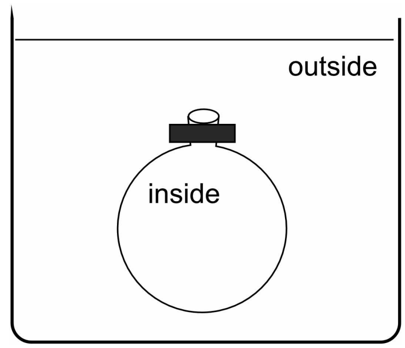
Exam #2 Chem 471 Fall 2001 Name:________________________

Work independently. Do not look at others' exams.
Do not allow your exam responses to be shared.

1. (25 points) Circle ALL correct answers, or fill in the blank, as appropriate.

You fill a (fixed volume) dialysis bag with a solution of your protein (1 mM) in water, seal the opening tightly, and place the bag into a much larger volume of pure water. The dialysis membrane is permeable to water, but not to your protein.

Answer the following sets of questions for two situations: I) immediately after you place the dialysis bag in the solution, before anything has happened and II) after an overnight incubation.



I. Initial Condition

a. The activity of the water outside is (**less than / equal to / greater than**) the activity of the water on the inside.
   greater than

b. The activity of the protein outside is (**less than / equal to / greater than**) the activity of the protein on the inside.
   less than

c. For the transfer of a small amount of water through the membrane from outside to inside, ΔG is (**less than zero** / **equal to zero / greater than zero**).
   less than zero

II. Final Condition

d. The activity of the water outside is (**less than / equal to / greater than**) the activity of the water on the inside.
   equal to

e. The activity of the protein outside is (**less than / equal to / greater than**) the activity of the protein on the inside.
   less than

f. For the transfer of a small amount of water through the membrane from outside to inside, ΔG is (**less than zero** / **equal to zero / greater than zero**).
   equal to zero

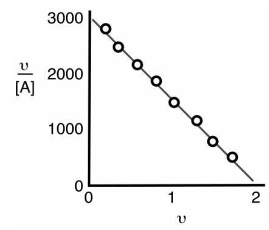
g. Assuming isothermal conditions and a fixed volume for the bag, what physical parameter inside the bag will change and how will it change?
   Pressure inside will increase

2. (25 points) As appropriate, either circle the correct answer or fill in the blank.

   a. If two aqueous solutions containing different nonvolatile solutes exhibit exactly the same vapor pressure at the same temperature, the activities of water in the two solutions (**are identical** / **might be different**) .

      Are identical (Chapt 5, Prob 16)

   b. For the data plotted at right, the ligand has __2_ independent, identical binding sites, each with a binding constant of ___**1500** $\mathbf{M^{-1}}$___.



      The x-intercept (2) provides the number of sites (N).
      The y-intercept (3000) is NK.
      You could also use the negative of the slope to calculate K, but use of the intercepts is easier.

   c. Liquid water at 100°C and 1 atm pressure is evaporated to water vapor at 100°C and 1 atm pressure. Considering all of the water to be the "system," (**ΔG / ΔH / ΔS**) is/are greater than zero.

      ΔH and ΔS

   d. System A contains 1.5 mM sucrose in water, while system B contains 1.5 mM protein in water. Both are at 25°C and 1 atm pressure. The activity of water in system B is (**less than / equal to / greater than**) the activity of water in system A.

      equal to

3. (20 points) Consider the ocean to be a 0.5 M NaCl solution, and consider a lake to be a 0.005 M $MgCl_2$ solution. Assume that both situations qualify as "dilute" and that the salts are completely dissociated.

See question 27, Chapter 5.

a. Which solution, the ocean or the lake, has the lower vapor pressure of water?

The ocean. More dissolved solutes means that the activity (mole fraction) of water is lower.

b. What is the osmotic pressure of ocean water in equilibrium with ***pure*** water?

Note that the NaCl in the lake water dissociates into TWO ionic species. So the total dissolved concentration of solutes is (2 x 0.5 M).

$$\Pi = cRT = (1.0M)(0.08205 \text{ atm } L\,K^{-1}\,mol^{-1})(298K) = 24.4\,atm$$

24.4 atm

c. To evaporate water from the lake and recondense it in the lake (transfer it from "lake to lake") requires no *net* energy. What is ΔG for the process of transferring 1 mol of pure water from the *lake* to the *ocean* at 25°C (and 1 atm pressure)?

$$\Pi_{lake} = cRT = (0.015M)(0.08205 \text{ atm } L\,K^{-1}\,mol^{-1})(298K) = 0.367\,atm$$

$$\Pi_{ocean} = cRT = (1.0M)(0.08205 \text{ atm } L\,K^{-1}\,mol^{-1})(298K) = 24.4\,atm$$

$$\Delta G = RT\ln\left(\frac{a_{H_2O(lake)}}{a_{H_2O(ocean)}}\right) = -(\Pi_{lake} - \Pi_{ocean})\bar{V}_A = -(0.367atm - 24.4atm)\left(\frac{mL}{0.99g}\ \frac{18.0g}{mol}\right)$$

$$= 437\frac{atm\,\text{mL}}{\text{mole}} = 437\frac{atm\,\text{mL}}{\text{mole}}\left(\frac{L}{10^3\,mL}\right)\left(\frac{8.314\frac{J}{\text{K}\ mole}}{0.08206\frac{L\text{ atm}}{\text{K}\ mole}}\right) = 43.9\frac{J}{mole}$$

4. (35 points) In the red blood cell, glucose is transported into the cell against its concentration gradient. The energy for this transport is provided by the hydrolysis of ATP:

ATP + H_2O ⇔ ADP + Pi (ΔG°' = -31 kJ mol^{-1})

Assume that the overall transport reaction is 100% efficient and given by:

ATP + H_2O 2glucose(out) ⇔ 2glucose(in) + ADP + Pi

a. At 25°C, under conditions where [ATP], [ADP], and [Pi] are each held constant at 1.0×10^{-2} M by cell metabolism, find the maximum value of $[glucose(in)]/[glucose(out)]$ Assume all activity coefficients are equal to 1.

ΔG°' for **glucose(out) ⇔ glucose(in)** is zero, so ΔG°' for the coupled reaction is the same as that for the simple ATP hydrolysis

$$\Delta G^{\circ\prime} = -31\text{ kJ mol}^{-1} = -RT\ln\frac{[glucose(in)]^2[ADP][Pi]}{[glucose(out)]^2[ATP](1)}$$

$$\frac{[glucose(in)]^2}{[glucose(out)]^2} = \frac{[ATP]}{[ADP][Pi]}e^{-\frac{\Delta G^{\circ\prime}}{RT}}$$

$$\frac{[glucose(in)]}{[glucose(out)]} = \sqrt{\frac{[ATP]}{[ADP][Pi]}e^{-\frac{\Delta G^{\circ\prime}}{RT}}}$$

$$= \sqrt{\frac{[ATP]}{[ADP][Pi]}e^{-\frac{-31000\,Jmol^{-1}}{(8.31\,Jmol^{-1}K^{-1})(298K)}}} = \sqrt{\frac{[ATP]}{[ADP][Pi]}e^{\frac{31000\,Jmol^{-1}}{(8.31\,Jmol^{-1}K^{-1})(298K)}}}$$

$$= \sqrt{\frac{[ATP]}{[ADP][Pi]}(2.73x10^5)} = \sqrt{\frac{10^{-2}}{10^{-2}10^{-2}}(2.73x10^5)} = 5200$$

b. In an actual cell, the glucose inside the cell may have an activity coefficient much less than 1 due to nonideal behavior. Would this increase or decrease the maximum concentration gradient obtainable? (Assume that all other activity coefficients are equal to 1).

If the activity coefficient is less than one, then the activity is less than the concentration. A higher concentration inside would be required to obtain the desired activity. The ration of in to out would increase.

Alternatively, using the math:

$$\frac{a_{glucose(in)}}{a_{glucose(out)}} = \frac{\gamma_{glucose(in)}[glucose(in)]}{\gamma_{glucose(out)}[glucose(out)]} = 5200$$

$$\frac{[glucose(in)]}{[glucose(out)]} = 5200\frac{\gamma_{glucose(out)}}{\gamma_{glucose(in)}} = \textit{for example} = 5200\frac{1.0}{0.9} > 5200$$