- 1. For each of the following systems, mark which of the choices make the statements true. Or, if it is not possible to determine, choose "can't determine".
  - a. (5 pts) 1:1 solution of benzene and toluene in equilibrium with its vapor.

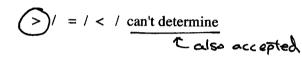
$$\mu$$
[benzene(vap)] ?  $\mu$ [toluene(vap)]

b. (5 pts)  $O_2$  at surface of Earth and  $O_2$ , 100 m above surface, in equilibrium:

$$\mu[O_2(g), surface] ? \mu[O_2(g), 100m]$$

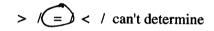
c. (5 pts) A solution of benzene with a small amount of dissolved solute.

 $\mu$ [pure benzene] ?  $\mu$ [benzene + solute]



d. (5 pts) Liquid water in equilibrium with air containing water vapor.

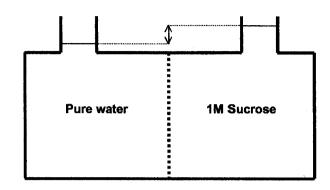
 $\mu[water(l)]$  ?  $\mu[water(vap)]$ 



e. (5 pts) Liquid water in the process of condensing (not equilibrium) from cool air to form dew.

 $\mu[water(1)]$  ?  $\mu[water(vap)]$ 

2. The containers pictured below are connected by a semipermeable membrane, which allows water to pass freely but blocks transport of sucrose. The tube diameters are 1 cm, their area is  $\pi(0.5)^2$  cm<sup>2</sup>, the height difference between liquid levels on each side is h (marked with the arrow), the density of both liquids is ~1 g/ml, and the total volume of the containers is large.



a. (5 pts) What is the pressure difference across the semipermeable membrane at equilibrium?

b. (5 pts) What height difference (h) between the liquid levels will result at equilibrium?

$$P = \frac{\pi}{A} = \frac{mg}{A} = \frac{R^{\frac{2}{1}} + R^{\frac{2}{1}}}{R^{\frac{2}{1}}} \Rightarrow \pi = \frac{R^{\frac{2}{1}} + R^{\frac{2}{1}}}{R^{\frac{2}1}} \Rightarrow \pi = \frac{R^{\frac{2}{1}} + R^{\frac{2}1}}{R^{\frac{2}1}} \Rightarrow \pi = \frac{R^{\frac{2}{1}} + R^{\frac{2}1}}{R^{\frac{2}1}} \Rightarrow \pi = \frac{R^{\frac{2}{1}} + R^{\frac{2}1}}{R^{\frac{2}1}} \Rightarrow \pi = \frac{R^{\frac{2}{1}} + R^{\frac{2}1}}{R^{\frac{2}1}}} \Rightarrow \pi = \frac{R^{\frac{2}{1}} + R^{\frac{2}1}}{R^{\frac{2}1}} \Rightarrow \pi = \frac{R^{\frac{2}{1}} + R^{\frac{2}1}}{R^{\frac{2}1}} \Rightarrow \pi = \frac{R^{\frac{2}{1}} + R^{\frac{2}1}}{R^{\frac{2}1}} \Rightarrow \pi = \frac{R^{\frac{2}1}}{R^{\frac{2}1}} \Rightarrow \pi = \frac{R^{\frac{2}1}}{R^{\frac{2}1}} \Rightarrow \pi = \frac{R^{\frac{2}1}}{R^{\frac{2}$$

process of pure water and 1M sucrose, initially at equal pressure, coming to equilibrium in the configuration pictured above.

$$W = \pi \overline{V} \Rightarrow \frac{W}{V} = \pi = \frac{24.5 \text{ atm}}{1 \text{ atm}} \cdot \frac{101.3 \text{ J/L}}{1 \text{ atm}} = \frac{2481}{1 \text{ atm}}$$

or solve with chanced potentials:

$$M_{L} = \mu_{120}^{0} + n_{H20} RT \ln (X_{H20})$$

$$M_{R} = \mu_{H20}^{0} + n_{H20} RT \ln (X_{H20}) + TTV$$
(H20)

$$M_L = M_R$$
 C equilibrium, so:

 $-n_{H_LO}$  RT In  $X_{H_{20},R} = + TT V = W$  = werk comes from the entropy of mixing!

 $\frac{W}{V} = TT = -n_{H_2O,R} RT In X_{H_2O,R} = (-55.6 \text{ mol})(.0821)(.298 \text{ k}) In (55.6)$ 
 $\frac{W}{V} = T = -n_{H_2O,R} RT In X_{H_2O,R} = (-4.3 \text{ q/m})$ 

24.5 q/m from (a)

3. You may find the following approximations useful:

$$\phi_0(\sigma) = \frac{\sigma L_D}{\varepsilon_w} \qquad L_D \approx \frac{10}{\sqrt{I}} nm$$

 $\phi_0$  = surface potential

 $L_D$  = Debye length

 $\mathcal{E}_{w}$  = dielectric constant of the water (this is a positive constant; you don't need its numerical value)

I = ionic strength (e.g. [NaCl]) in units of mM

 $\sigma$  = surface charge density in units of charge per area

A membrane protein (in a membrane) binds a negatively charged, soluble ligand (L2):

$$P + L^2 \leftarrow K_{eq} \rightarrow PL^2$$
  $\Delta G = \Delta G^0 + RT \ln Q - 2F \phi_0$ 

a. (10 pts) You measure  $K_{eq}$  for this reaction in negatively charged membranes (e.g.  $\sigma < 0$  so  $\phi_0 < 0$ ) how will changing the ionic strength affect  $K_{eq}$ ? Justify your answer quantitatively with appropriate equations

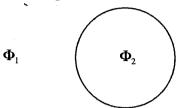
antitatively with appropriate equations
$$\Delta G = 0 \Rightarrow \text{ keq} = e^{-\Delta G^{\circ}} \quad e^{2F\phi_{\circ}}$$

Problem continues on next page ...

- 3. (continued) Suppose you discover a mutant ligand that binds with the same  $\Delta G^{\circ}$  but exists as a heterodimer (LX), which is net neutral:  $P + (LX) \rightarrow P(LX)$
- b. (7.5 pts) Write an expression for  $\Delta G$  of this reaction.

c. (7.5 pts) Under what conditions, if any, would you expect the equilibrium binding constant of the mutant ligand,  $K_{eq}$  (mutant), to be the same as  $K_{eq}$  for the regular ligand? (Explain with appropriate equations)

4. Consider a lipid vesicle, which consists of a spherical lipid membrane enclosing a volume of solution as pictured below. The electrostatic potential outside the vesicle,  $\Phi_1$ , differs from the electrostatic potential inside,  $\Phi_2$ .



a. (5 pts) Suppose an ion channel in this vesicle's membrane allows Na<sup>+</sup> ions to pass freely. Using the Boltzmann equation, write an expression that relates the concentration of Na<sup>+</sup> ions inside and outside the vesicle at equilibrium.

$$[Na^{\dagger}]_{out} = [Na^{\dagger}]_{in} e^{\frac{2\pi V}{RT}}$$
  $V = \phi_2 - \phi_1$ 

b. (10 pts) Derive the expression you gave in part (a) from chemical potentials. Hint: all you need to do is write down the correct chemical potentials, apply the appropriate equilibrium condition, and with a couple algebraic steps you will have it.

Min = 
$$M^0$$
 + RT In [Nat] in +  $2f \phi_2$   
Mout =  $M^0$  + RT In [Nat] out +  $2F \phi_1$   
 $\Delta M = RT In [Nat] in +  $2F (\phi_2 - \phi_1) = 0$  @ equilibrium  
 $In [Nat] in = \frac{2F}{2T} (\phi_2 - \phi_1)$   
[Nat] in =  $[Nat]_{in} = \frac{2F(\phi_2 - \phi_1)}{RT}$$ 

c. (10 pts) Suppose the membrane surface has a negative surface potential of  $\Phi_0 = -75$  mV (e.g. $\Phi$  at membrane surface =  $\Phi_1$  - 75 mV for the outer surface and for the inner surface ...). Under what circumstances would this surface potential effect [Na<sup>+</sup>] inside the vesicle? Hint: Equations given in problem 3 are useful and use equations to justify your answer.

 $\phi_0$  will only affect [Nat] within the Debye Length, LD, which depends on the ionic strength of the solution:  $L_D = \frac{10}{\sqrt{11}}$ 

If the radius of the reside is larger than the Debye length, the TNat] will only be affected within the Debye length. If the radius is similar to or smaller than the Lo, [Nat] will increase in the reside.