NAME:

1. For each of the following closed systems, mark which conditions are true, which are not necessarily true, and which cannot be true.

a. (5 pts) Ice in equilibrium with air (containing a trace of water vapor) at –40 °C.

$\mu[H_2O(s)] = \mu[H_2O(vap)]$ [✓ true] / not necessarily true / cannot be true

b. (5 pts) Solid sucrose in the process of crystallizing (spontaneously) from an aqueous sucrose solution:

$\mu[\text{sucrose(s)}] > \mu[\text{sucrose(aq)}]$ true / not necessarily true / [✓ cannot be true]

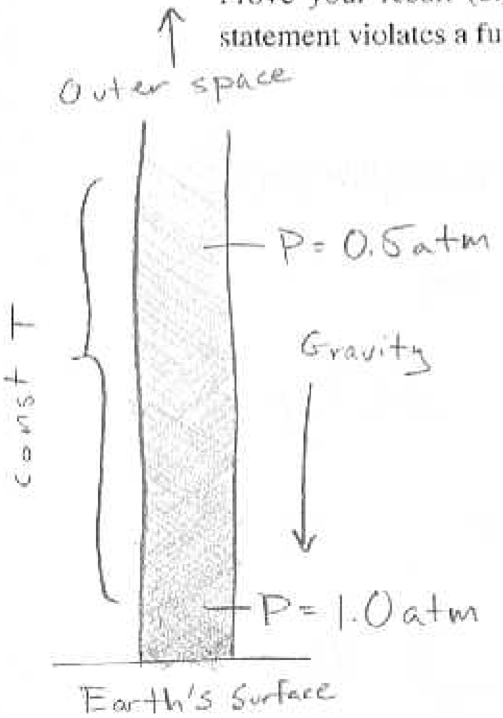
c. (5 pts) An equilibrium phase separated mixture of water and decane.

$\mu[\text{water}] = \mu[\text{decane}]$ true / [✓ not necessarily true] / cannot be true

d. (10 pts) Air at 1 atm pressure in equilibrium with air at 0.5 atm pressure.

[✓ possible] / not possible

Prove your result (e.g. describe a system that achieves this or demonstrate that the statement violates a fundamental law of thermodynamics)



If there is an external field to counteract the pressure gradient, then air at different pressures can be in equilibrium, even at the same temperature.

NAME:

2. Assume the deepest part of the ocean is 10,000 m deep and each 10 m of water adds 1 atm of pressure. You may need $\Delta\overline{H}_{vap} = 40.7$ kJ/mol for water and vapor pressure of pure water = 1 atm at 100 °C and 1 atm external pressure.

a. (5 pts) What is the pressure at the bottom of the ocean?

$$1\,\text{atm} + \frac{10000\,\text{m}}{10\,\text{m}/\text{atm}} = 1001\,\text{atm}$$

b. (10 pts) At what temperature will pure water boil at the bottom of the ocean?

$$\ln\frac{P_2}{P_1} = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\frac{1001}{1} = \frac{-40700\,\text{J}/\text{mol}}{8.314\,\text{J}/(\text{K}\cdot\text{mol})}\left(\frac{1}{T_2} - \frac{1}{373\,\text{K}}\right)$$

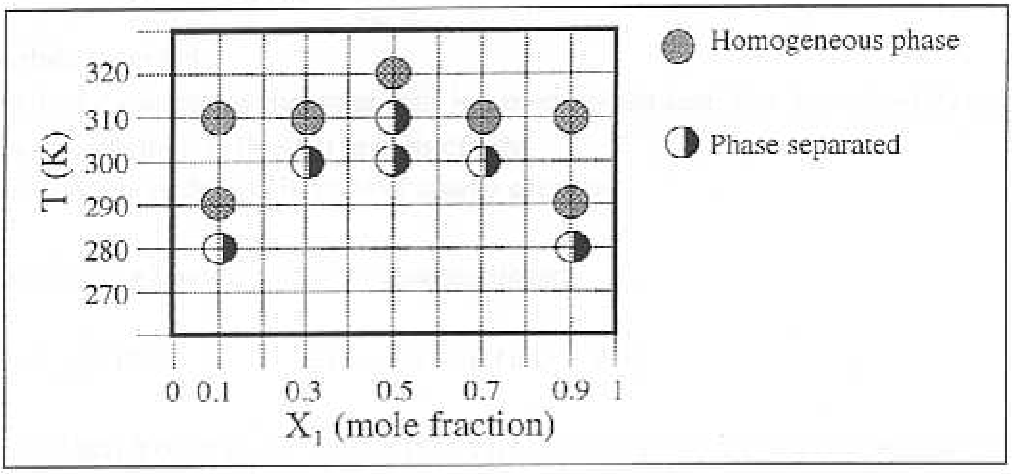
$$T_2 = 788\,\text{K}.$$

c. (5 pts) Will sea water also boil at this temperature and pressure? (Explain)

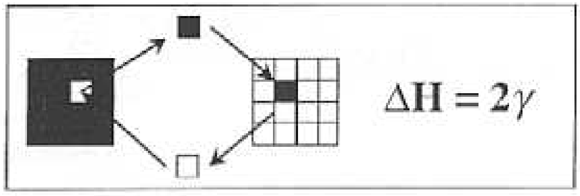
No. Sea water is a solution. So the solutes will lower the vapor pressure so T_b will be higher in order to get $P_{vap} = P_{ext}$.

NAME:

3. Consider the following experimental results. Various mixtures of component 1 and 2 are prepared at various temperatures. The mixtures are examined and the results of whether they were homogeneous or phase separated are recorded.



a. (10 pts) Based on these results, what is the sign of ΔH for the process of swapping one molecule of 1 with one molecule of 2 in otherwise pure states? Be sure to justify your answer.



ΔH + b/c if it was negative, mixing would occur for all temperatures

or ΔG_{mix} needs to be (+)

$$\Delta G_{mix} = \underset{\text{must be}(+)\text{ for }\Delta G(+)}{\Delta H_{mix}} - T\overset{\text{always }(+)}{\Delta S_{mix}}$$

b. (10 pts) Using the data given above, calculate the value of this ΔH in kJ/mol?

$\gamma = 2 k_B T_c \qquad T_c \approx 310\ k$

$\Delta G = 2\gamma = 4 k_B T_c$

$\overline{\Delta G} = 4 k_B T_c \tilde{N}_A = 4 R T_c = 4(8.314)\,310 = 10.3\ ^{kJ}/_{mol}$

NAME:

4. In class, we derived the following useful approximations:

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

ϕ_0 = surface potential

ε_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

σ = surface charge density in units of charge per area

A membrane protein binds a positively charged ligand:

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

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.

$$K_{eq} = e^{-(\Delta G + 2F\phi_0)/RT} = \underbrace{e^{-\frac{\Delta G}{RT}}}_{\text{constant}} e^{-\frac{2F\phi_0}{RT}} \qquad \phi_0 < 0$$

$$\phi_0 = \frac{\sigma L_D}{\varepsilon_w} \approx \frac{10\sigma}{\varepsilon_w \sqrt{I}}$$

as I Increases, $|\phi_0|$ decreases & K_{eq} decreases

as I decreases, $|\phi_0|$ increases & K_{eq} increases

The negative electrical potential favors this reaction, so increasing the magnitude of this will increase K_{eq}. Lowering ionic strength increases ϕ_0 and will increase K_{eq}.

Problem continues on next page ...

NAME:

4. (continued) Suppose you discover a mutant ligand that binds with the same $\Delta G°$ but exists as a dimer $(LL)^{4+}$ so the binding reaction is: $P + (LL)^{4+} \rightarrow P(LL)^{4+}$

b. (7.5 pts) Write an expression for ΔG of this reaction.

$$\Delta G = \Delta G^\circ + RT\ln Q + 4F\phi_\circ$$

c. (7.5 pts) Under what conditions, if any, would you expect the equilibrium binding constant of the mutant ligand, $K_{eq}(2)$, to be the same as K_{eq} for the regular ligand? (Explain)

$$K_{eq} = e^{-(\Delta G^\circ + 2F\phi_\circ)/RT} \qquad K_{eq}(2) = e^{-(\Delta G^\circ + 4F\phi_\circ)/RT}$$

$K_{eq}(2) = K_{eq}$ when the membrane potential $\phi_\circ = 0$ since we are given that ΔG°'s are equal

d. (10 pts) Derive an expression for $K_{eq}(2)$, in terms of K_{eq} for the regular ligand.

@ equilibrium

$$\Delta G^\circ = -RT\ln K_{eq} + 2F\phi_\circ$$

$$\Delta G^\circ = -RT\ln K_{eq} + 4F\phi_\circ$$

$$K_{eq} = e^{-(\Delta G^\circ + 2F\phi_\circ)/RT}$$

$$K_{eq}(2) = e^{-(\Delta G^\circ + 4F\phi_\circ)/RT}$$

$$K_{eq}(2) = e^{-(\Delta G^\circ + 2F\phi_\circ + 2F\phi_\circ)/RT}$$

$$K_{eq}(2) = K_{eq}\, e^{-2F\phi_\circ/RT}$$