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 water:

   $\mu[H_2O(s)] = \mu[H_2O(l)]$ [✓ true] / not necessarily true / cannot be true (+5)

   b. (10 pts) Solid sucrose in the process of dissolving into an aqueous sucrose solution that is currently 50% saturated:

   $\mu[\text{sucrose}(s)] > \mu[\text{sucrose}(aq)]$ [✓ true] / not necessarily true / cannot be true (+5)

   $\mu[H_2O(\text{pure liq.})] = \mu[H_2O(\text{sucrose sol.})]$ true / not necessarily true / [✓ cannot be true] (+5)

   c. (10 pts) Ice in equilibrium with an aqueous solution of sucrose:

   $\mu[\text{sucrose}(\text{ice})] = \mu[\text{sucrose}(aq)]$ [✓ true] / not necessarily true / cannot be true (+5)

   $[\text{sucrose}](\text{ice}) = [\text{sucrose}](aq)$ true / [✓ not necessarily true] / cannot be true (+5)
   (here [...] denotes concentration)

2. Suppose a gas containing CO_2 at a mole fraction of 0.01 is in equilibrium with liquid water at 25 °C. Henry's constant for CO_2: $k(CO_2, 25\ °C) = 1.6 \times 10^3$ atm

a. (10 pts) Calculate the equilibrium mole fraction of CO_2 dissolved in the water at 1atm.

Using Henry's Law: $P_{CO_2} = X^{aq}_{CO_2} K_{CO_2}$

$P_{CO_2} = P_{Total} X_{CO_2} = 1 \cdot .01 = .01$

$.01 = X^{aq}_{CO_2} \cdot 1.6 \cdot 10^{3}$

$$\boxed{X^{aq}_{CO_2} = 6.3 \cdot 10^{-6} = \frac{\text{moles } CO_2}{\text{moles } CO_2 + \text{moles } H_2O}}$$

b. (10 pts) What is the molarity of CO_2 in the water at equilibrium with this gas at 10 atm pressure?

at 10 atm $P_{CO_2} = .1 = X^{aq}_{CO_2} K_{CO_2}$

$X = \frac{n_{CO_2}}{n_{CO_2} + n_{H_2O}}$

$X^{aq}_{CO_2} = 6.3 \cdot 10^{-5}$

This is the mole fraction.
To get moles / liter...

Assume $X^{aq}_{CO_2}$ small compared to moles H_2O in 1 ℓ (it is)

From data on front page: 55.6 mole H_2O/ℓ

[redacted]

$$\boxed{[CO_2] = \underbrace{6.3 \cdot 10^{-5}}_{X^{aq}_{CO_2}} \cdot \underbrace{55.6}_{\text{Total \# moles in } 1\ell} = 3.5 \cdot 10^{-3} \text{ mol/liter}}$$

3. A cell membrane at 37 °C is found to be permeable to Ca^{2+} but not to anions, and analysis shows the inside concentration to be 70 mM and the outside concentration to be 5 mM in Ca^{2+}.

(25 pts) What potential difference must exist across the membrane for Ca^{2+} to be in equilibrium at the stated conditions? You may assume activity coefficients are equal to 1 and you must give the sign of the potential inside with respect to that outside.

$[Ca^{2+}] = .07$ | $[Ca^{2+}] = .005$

Φ_{in} | Φ_{out}

$$\mu_{in} = \mu^\circ + RT\ln\left(\frac{C_{in}}{1M}\right) + zF\Phi_{in}$$

$$\mu_{out} = \mu^\circ + RT\ln\left(\frac{C_{out}}{1M}\right) + zF\Phi_{out}$$

At equilibrium $\underline{\mu_{in} = \mu_{out}}$

$$\mu^\circ + RT\ln\left(\frac{C_{in}}{1M}\right) + zF\Phi_{in} = \mu^\circ + RT\ln\left(\frac{C_{out}}{1M}\right) + zF\Phi_{out}$$

$$zF(\Phi_{in} - \Phi_{out}) = RT\ln\left(\frac{C_{out}}{C_{in}}\right)$$

$$\Phi_{in} - \Phi_{out} = \frac{RT}{zF}\ln\left(\frac{C_{out}}{C_{in}}\right)$$

$$\Phi_{in} - \Phi_{out} = \frac{(8.314)(310)}{(2)(96,487)}\ln\left(\frac{.005}{.07}\right)$$

(-2.64)

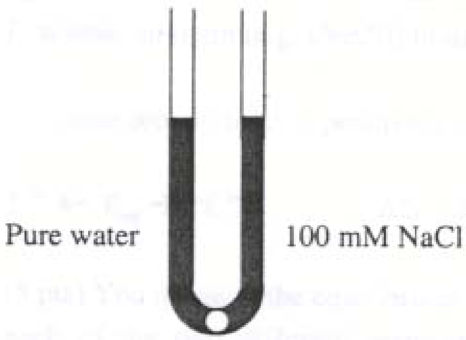
$$\boxed{\Phi_{in} - \Phi_{out} = -0.035\ V}$$

Φ_{in} is 35mV <u>negative</u> with respect to Φ_{out}

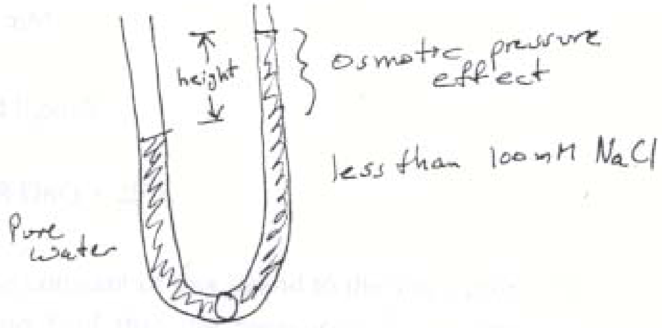
4. A glass tube is filled with water except for a small drop of liquid that is immiscible with water. This liquid allows passage of water, but not ions (it is a semipermeable barrier). Initially, the left side of the tube is filled with 100 ml of pure water and the right side is filled with 100 ml of 100 mM NaCl.

a. (10 pts) If the droplet is fixed in place, sketch the equilibrium state of the system.

(initial state)

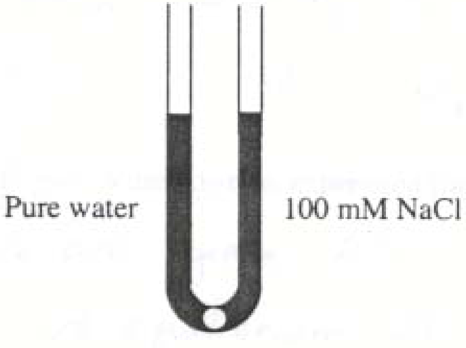


(equilibrium state)

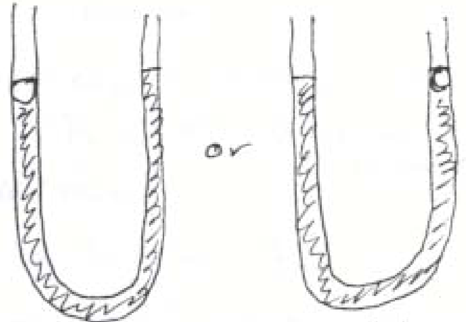


b. (10 pts) Sketch the equilibrium state of this system if the drop is free to move (assume the drop, pure water, and 100 mM NaCl all have the same density).

(initial state)



(equilibrium state)



equilibrium is completely mixed

c. (10 pts) What pressure difference between the two sides would be necessary for the initial state to be at equilibrium? Which side must be under higher pressure?

More pressure must be exerted on 100 mM NaCl side to maintain equilibrium.

$\Pi = cRT$ ← Assume T = 298 K

$= 0.1 \cdot$ [redacted] $\cdot 298 = 2.45$ atm

.08205

5. (*Extra Credit*) Consider two lipid membranes which have surface charge densities of σ_1 and σ_2, respectively. 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 of the membrane (ϕ_0 is different for the 2 membranes)

ε_w = dielectric constant of the water (this is positive constant; you don't need its numerical value)

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

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. (5 pts) You measure the equilibrium binding constant of this ligand to the same protein in each of the two different membranes and find that the measured K_{eq} is <u>larger in membrane 2</u> than in membrane 1. What can you deduce about the relation of σ_1 and σ_2? (Hint: this does not require the answer to part b, but if you are stuck, try doing b first.)

Adding ⊕ charge to membrane 2 must be easier than adding ⊕ charge to membrane 1.

$\sigma_2 < \sigma_1$ since energy $\propto$ (charge) × Φ_0 and $\Phi_0 \propto \sigma \Rightarrow$ lower σ = lower energy

b. (5 pts) Write down an expression for K_{eq} in terms of ΔG^0 and ϕ_0.

We are given $\Delta G = \Delta G^\circ + RT\ln Q + 2F\Phi_0$

at equilibrium $\Delta G = 0 \Rightarrow 0 = \Delta G^\circ + RT\ln K_{eq} + 2F\Phi_0$

$$RT\ln K_{eq} = -\Delta G^\circ - 2F\Phi_0$$

$$K_{eq} = e^{-(\Delta G^\circ + 2F\Phi_0)/RT}$$

c. (5 pts) Will increasing the ionic strength in solution make the measured K_{eq} values in the two membranes more similar or more different? (please explain briefly)

Increasing ionic strength will decrease L_D and since $\Phi_0 \propto \sigma L_D$, this will also decrease Φ_0 and <u>reduce</u> differences between membranes