Physics 112, Fall 2017: Holzapfel
Problem Set 11 (6 Problems). **Due Friday, December 1, 5PM**

Problem 1: **Partial Pressure**
Suppose you have a liquid in equilibrium with its gas phase inside a closed container that is in contact with a thermal reservoir. You then pump in an inert gas raising the pressure exerted on the liquid. Does the fraction of the liquid in the vapor phase decrease or increase?

a) Use the definition of the Gibbs free energy in terms of the chemical potential and the assumption that the vapor phase is an ideal gas to show that the chemical potential depends on the pressure in the following way:

$$\mu(T,P) = \mu(T,P_0) + k_b T \ln\left(\frac{P}{P_0}\right).$$

b) For the liquid to remain in diffusive equilibrium with its gas phase, the chemical potentials of each must change by the same amount when the inert gas is introduced. Use this fact, combined with the result of part (a), to derive a differential equation for the equilibrium vapor pressure, P_v, as a function of the total pressure, P. Treat the gases as ideal and assume that none of the inert gas dissolves in the liquid.

c) Solve the differential equation found in part (b) to show that:

$$P_v(P) = P_v(P_v)\exp\left[\frac{(P-P_v)}{n_l kT}\right]$$

where n_l is the number density of the liquid phase and $P_v(P_v)$ is the vapor pressure in the absence of the inert gas. Thus, the presence of the inert gas leads to a slight increase in the vapor pressure: it causes more liquid to evaporate.

d) Calculate the fractional increase of vapor pressure when air corresponding to one atmosphere of pressure is added to a system of water and water vapor in equilibrium at 300K. Over what range of conditions will the changes in the vapor pressure be negligible?

Problem 2: **Boiling temperature of water as a function of altitude**
Assume that the atmosphere is isothermal, and that it falls off exponentially with altitude as we found earlier this semester

$$P = P_0 \exp\left(\frac{-mgh}{k_b T}\right).$$

where P_0 is the atmospheric pressure at sea level.
In problem #1 you showed that under normal conditions the vapor pressure of water is little effected by the presence of the inert atmospheric components. The vapor pressure of the water is given by

$$P = C \exp\left(\frac{-L}{RT_w}\right)$$

where $R = k_b N_A$ and C is a constant. The molar heat of vaporization is relatively constant over the temperature range from 50 to 100°C and has the value $L \sim 50$kJ/mole.

a) Assume that when the vapor pressure of the water becomes equal to the atmospheric pressure, the water begins to boil. Show that the temperature at which the liquid boils as a function of the altitude, h, is given by:

$$T_b = \frac{T_{b0}}{1 + \frac{T_{b0}}{T_a}\frac{mghN_A}{L}}.$$

where m is the mass of a nitrogen molecule and T_{b0} is the boiling temperature at atmospheric pressure.

b) Use the chain rule to calculate the change in boiling temperature for small changes in altitude: $dT_b/dh = (dT_b/dP)(dP/dh)$. Show that the result of part (a) is equivalent to this result for small changes in altitude.

c) Use your result from part (a) to estimate the temperature at which water boils on the summit of Mount Whitney (4417 meters). What implications could this have for high altitude cooking?

Problem 3: **Osmotic Pressure**
Seawater has a salinity of 3.5% meaning that if you boil away a kilogram of seawater, there will be 35g of solids (mostly NaCl). When dissolved, the Sodium Chloride dissociates into separate Na^+ and Cl^- ions.

a) Calculate the osmotic pressure difference between seawater and fresh water. For simplicity, assume that all the dissolved salts in seawater are NaCl.

b) Reverse osmosis occurs when you apply a pressure difference greater than the osmotic pressure to a solution separated from a pure solvent by a membrane permeable only to the solvent. In this process, the solvent flows out of the solution and this can be used to desalinate sea water. Use your result from Part (a) to find the minimum work required to desalinate one liter of water.

c) It is also possible to desalinate water by evaporation. The water vapor is recondensed and the salt is left behind. Compare your result from part (b) with the amount of heat that would be required to evaporate a liter of water. Assume that the water starts at a temperature of 300 K and the latent heat of vaporization at a pressure of one atmosphere is 40.7 kJ/mol. Compare your result with that of Part (b).

Problem 4: **Boiling and Freezing**
At atmospheric pressure, pure water boils at 100 C, and freezes at 0 C. In this problem, we calculate how this changes for seawater.

a) Use the latent heat of vaporization and salinity given in problem #4 to calculate the boiling temperature of seawater at atmospheric pressure.

b) At atmospheric pressure, the latent heat of fusion for ice is 6.0 kJ/mol. Use this information to calculate the freezing temperature of water. Assume that when the solution freezes, it forms a phase of pure ice.

c) In part (a), the boiling temperature is increased by the addition of salt. However, in part (b) the freezing temperature is decreased. Using what you know about the entropy of mixtures, explain why this is the case.

Problem 5: **Purifying solids**
Let B be an impurity in A, with $x = N_B/(N_B + N_A) << 1$. In this limit, the free energy changes not due to mixing can be expressed as a linear functions of x, as $f(x) = f(0) + xf'(0)$, for both liquid and solid phases. Assume that the liquid mixture is in equilibrium with the solid mixture. Calculate the equilibrium concentration ratio $k = x_S/x_L$, called the segregation coefficient. For many systems $k << 1$, and then the substance may be purified by melting and partial resolidification, discarding a small fraction of the melt. This principle is widely used in the purification of materials, as in the zone refining of semiconductors. Give a numerical value for k for $f'_S - f'_L = 1\,eV$ and $T = 1000$ K.

Problem 6: **Vapor Pressure**
a) Consider a solvent with a small fraction of solute $x << 1$. Using an argument similar to that used in class to derive expression for the change in boiling temperature, show that the vapor pressure of the solution is

given by

$$P = P_0(1 - x)\,.$$

b) The result in Part (a) represents a decrease in vapor pressure of the solvent when solute is added and the temperature is held constant. However, the Clausis-Clapeyron equation tells us that for the pure solvent, a decrease in pressure would lead to a corresponding decrease in the boiling temperature. Show that the reason the pressure can change, but not the boiling point, is that the addition of the solute increases the boiling temperature of the solution the amount necesssary to cancel the decrease from the Clausius-Clayperon equation.