

Physics 112 Fall 2017
Professor William Holzapfel
Homework 11 Solutions

Problem 1. Partial Pressure

(a) We can write the Gibbs free energy in two ways,

$$G = \mu N = U - \tau\sigma + pV,$$

so dG is:

$$\begin{aligned} dG &= dU - \tau d\sigma - \sigma d\tau + p dV + V dP \\ &= \mu dN + N d\mu. \end{aligned}$$

Using the thermodynamic identity $dU = \tau d\sigma - p dV + \mu dN$ and noting that $dV = d\tau = 0$ for an isothermal process at constant volume in this problem, this reduces to:

$$d\mu = \frac{V}{N} dp. \quad (1)$$

The above relation is quite general and holds for any system undergoing an isothermal process at constant volume. Note that both the liquid and the gas in our problem really do have constant volume; If we assume the liquid is essentially incompressible then the volume of the liquid is approximately constant, which implies that the volume of both the vapor and the inert gas will also be constant since the total volume is constant.

(b) Consider the liquid by itself. The relevant pressure is the *total* pressure p on the liquid, due to both the vapor pressure and the pressure of the inert gas. From (1) we have

$$d\mu_l = \frac{V_l}{N_l} dp = \frac{1}{n_l} dp.$$

Applying (1) to the vapor and invoking the ideal gas law gives

$$d\mu_v = \frac{V_v}{N_v} dp_v = \frac{\tau}{p_v} dp_v.$$

Because the liquid and vapor are in equilibrium $d\mu_v = d\mu_l$, so we have the differential equation:

$$\frac{dp}{n_l} = \tau \frac{dp_v}{p_v}.$$

(c) We can integrate the above equation for $p_v = P_0 \rightarrow P_v$ and $p = P_0 \rightarrow P$

$$\int_{P_0}^P \frac{dp}{n_l} = \int_{P_0}^{P_v} \tau \frac{dp_v}{p_v} \quad (2)$$

$$\implies \frac{P - P_0}{n_l} = \tau \ln(P_v/P_0). \quad (3)$$

Solving this for the vapor pressure of the liquid P_v as a function of the total pressure P above the liquid we have:

$$P_v(P) = P_0 \exp \left(\frac{P - P_0}{n_l k_b T} \right). \quad (4)$$

(d) Since the additional gas pressure $\Delta P = P - P_0 = 1$ atm and the number density of water is:

$$n_l = 10^3 \text{ kg/m}^3 \times \frac{1}{18 \times 1.6 \times 10^{-27} \text{ kg}} \frac{1}{\text{kg}} \approx 3.47 \times 10^{28} \text{ 1/m}^3$$

we can calculate the fractional change in vapor pressure:

$$\begin{aligned} \frac{P_v(P)}{P_0} &= \exp \left(\frac{P - P_0}{n_l k_b T} \right) = \exp \left(\frac{10^5 \text{ Pa}}{(3.47 \cdot 10^{28} \text{ 1/m}^3) (1.38 \cdot 10^{-23} \text{ J/K}) (300 \text{ K})} \right) \\ &\approx e^{7 \cdot 10^{-4}} = 1.0007. \end{aligned}$$

This is pretty small. By (4), this fractional change will be insignificant until

$$\Delta p \sim n_l k_b T \approx 10^3 \text{ atm}. \quad (5)$$

Since this greater than 1 atm, this tells us that we can safely neglect the effects of inert gases on the vapor pressure of water at any point in the atmosphere! We'll need this conclusion in problem 2.

Problem 2: Boiling Temperature of water as a function of altitude

(a) The boiling point is when the vapor pressure is equal to the atmospheric pressure, and setting these equal gives

$$p_0 \exp \left(-\frac{mgh}{k_b T_a} \right) = C \exp \left(-\frac{L}{k_b N_A T_b} \right). \quad (6)$$

We can find the constant C by evaluating this at at sea level ($h = 0$) in terms of the sea level boiling temperature T_{b0} :

$$C = p_0 \exp \left(\frac{L}{k_b N_A T_{b0}} \right).$$

Plugging this into (6) and solving for T_b gives:

$$T_b = \frac{T_{b0}}{1 + \frac{T_{b0}}{T_a} \frac{mgh N_A}{L}}. \quad (7)$$

(b) First we can calculate $\frac{dT_b}{dh}$ directly from (7):

$$\begin{aligned} \frac{dT_b}{dh} &= \frac{d}{dh} \left(\frac{T_{b0}}{1 + \frac{T_{b0}}{T_a} \frac{mgh N_A}{L}} \right) = - \frac{1}{\left(1 + \frac{T_{b0}}{T_a} \frac{mgh N_A}{L} \right)^2} \cdot \frac{T_{b0}^2 m g N_A}{T_a L} \\ &= - \frac{T_b^2}{T_a} \frac{m g N_A}{L} \end{aligned} \quad (8)$$

where we've written our result in terms of T_b rather than h since it gives a neater expression. To calculate $\frac{dT_b}{dh} = \frac{dT_b}{dp} \frac{dp}{dh}$ using the chain rule, we must first invert the given relationship between vapor pressure and temperature, yielding

$$T_b(p) = -\frac{L}{R \ln(p/C)} \quad (9)$$

$$\Rightarrow \frac{dT_b}{dp} = \frac{L}{pR \ln(p/C)^2}. \quad (10)$$

We also have

$$\frac{dp}{dh} = \left(-\frac{mg}{k_b T_b}\right) p_o e^{-\frac{mgh}{k_b T_b}} = \left(-\frac{mg}{k_b T_b}\right) p.$$

Putting this all together yields

$$\begin{aligned} \frac{dT_b}{dh} &= \frac{dT_b}{dp} \frac{dp}{dh} = -\frac{mgL}{RkT_a \ln(p/C)^2} \\ &= -\frac{T_b^2}{T_a} \frac{mgN_A}{L} \end{aligned}$$

in agreement with (8). In the third equality we used (9) to eliminate $\ln(p/C)$.

(c) Using (7) and plugging in gives

$$\begin{aligned} T_b &= \frac{373 \text{ K}}{1 + \frac{373 (28 \times 1.66 \times 10^{-27})(9.8)(4417)(6.02 \times 10^{23})}{293 \cdot 50 \times 1000}} \\ &\approx 361.8 \text{ K}. \end{aligned}$$

Because the boiling point at high altitudes is reduced by over 10° C, cooking with boiling water will take longer.

Problem 3: Osmotic Pressure

(a) The osmotic pressure between a solution with a number density n of impurities and the pure liquid is

$$\Delta P = P_s - P_l = n\tau. \quad (11)$$

If the salinity is 3.5%, the number density of the impurities is (remembering that each NaCl gives two ions):

$$n = 2 \frac{\rho}{m_{NaCl}} = 2 \frac{35 \text{ g/L} \times 10^3 \text{ L/m}^3 \times 6.02 \cdot 10^{23}}{(23 + 35.5) \text{ g}/N_A} = 7.2 \times 10^{26} \frac{1}{\text{m}^3}$$

so the pressure difference is:

$$\Delta P = \left(7.2 \times 10^{26} \frac{1}{\text{m}^3}\right) (300 \text{ K})(1.38 \times 10^{-23} \text{ J/K}) \approx 3 \times 10^6 \text{ Pa} \sim 30 \text{ atm}.$$

(b) To extract the water by reverse osmosis, we need to apply pressure $P > \Delta P = 3 \times 10^6$ Pa. If the initial volume of salt water is finite then the concentration will increase as we push

water through the membrane, and the required pressure will increase as per (11). In the limit of an infinite volume of salt water, however, the concentration will *not* change as we push one liter of water through the membrane, and thus the required pressure stays constant at $\Delta P = 3 \times 10^6$ Pa. Since the pressure does not increase this is the minimum work scenario, and that work is given by

$$W_{\min} = P\Delta V = (3 \times 10^6 \text{ Pa}) (1 \text{ L} \times 10^{-3} \text{ m}^3/\text{L}) \approx 3 \text{ kJ}.$$

(c) We'll ignore the small change in boiling point of seawater (that's problem 2) to calculate the heat required to heat the water from 300 K to boiling (373 K):

$$Q = C_v \Delta T = (10^3 \text{ g} \cdot 1 \text{ cal/g} \cdot \text{K} \cdot 4.18 \text{ J/cal}) (73 \text{ K}) \approx 305 \text{ kJ}$$

and the heat required to boil all the water is:

$$Q = Lm = 40.7 \text{ kJ/mol} \cdot \frac{1}{18} \text{ mol/g} \cdot 10^3 \text{ g} = 2,260 \text{ kJ}.$$

So the total energy require to desalinate the water by evaporation is $\sim 2.6 \cdot 10^6 \text{ J}$ which is $\sim 1,000$ times the energy required for desalination by reverse osmosis.

Problem 4: Boiling and Freezing

(a) In lecture we found the change in boiling temperature of a solution due to the presence of impurities to be $\Delta T = \frac{RT_0^2}{L}x$ where x is the concentration of impurities $x \equiv \frac{N_{\text{imp}}}{N_{\text{solvent}}}$ and R is the gas constant. For seawater with 3.5% salinity (35 g NaCl per 1000 g seawater), the concentration is:

$$x = \frac{2N_{\text{NaCl}}}{N_{\text{H}_2\text{O}}} = \frac{2 \frac{35 \text{ g}}{(23+35.5) \text{ g}/N_A} (6.02 \cdot 10^{23})}{\frac{965 \text{ g}}{18 \text{ g}/N_A} (6.02 \cdot 10^{23})} = 0.022.$$

The boiling point of seawater is then:

$$T_b = T_0 + \frac{RT_0^2}{L}x = 100^\circ \text{ C} + \frac{(8.31 \text{ J/K} \cdot \text{mol}) (373 \text{ K})^2}{40.7 \text{ kJ/mol}} (0.022) = 100.62^\circ \text{ C}.$$

(b) When water freezes it releases heat, so the latent heat of the water \rightarrow ice transition is $L = -6.0 \text{ kJ/mol}$, and thus

$$T_f = T_0 + \frac{RT_0^2}{L}x = 0^\circ \text{ C} + \frac{(8.31 \text{ J/K} \cdot \text{mol}) (273 \text{ K})^2}{-6.0 \text{ kJ/mol}} (0.022) = -2.3^\circ \text{ C}.$$

(c) The reason that the boiling temperature goes up while the freezing temperature goes down is because the liquid phase is the only mixed phase. The mixing increases the entropy

of the liquid phase, making it entropically more favorable, and so the system prefers to be in that phase. Thus there is an increase in the temperature range over which the system is liquid, with an elevation of the boiling point and a depression of the freezing point.

Problem 5: Purifying Solids

Consider the solid and liquid phases of a mixture with N_l and N_s total atoms in the liquid and solid phases respectively, as well as impurity concentrations x_s and x_l . From Kittel equation 3.80 we know that the entropy of mixing in the liquid is

$$\begin{aligned}\sigma_{l,\text{mix}}(x_l) &= -N_l [(1 - x_l) \ln(1 - x_l) + x_l \ln x_l] \\ &\approx -N_l x_l (1 - \ln x_l)\end{aligned}$$

where we've made a couple of approximations using $x_l \ll 1$. A similar expression holds for the entropy of the mixing in the solid. Dividing by the number of atoms in the phase, we obtain the specific entropy of mixing for the liquid and the solid

$$\begin{aligned}s_{l,\text{mix}}(x_l) &= x_l (1 - \ln x_l) \\ s_{s,\text{mix}}(x_s) &= x_s (1 - \ln x_s).\end{aligned}$$

We are told that for each phase the free energy per particle NOT due to mixing can be written in the form $f(0) + x f'(0)$, so combining this with the previous equation gives

$$\begin{aligned}f_l(x_l) &= f_l(0) + x_l f'_l(0) - \tau x_l (1 - \ln x_l) \\ f_s(x_s) &= f_s(0) + x_s f'_s(0) - \tau x_s (1 - \ln x_s)\end{aligned}$$

As explained in Chapter 11 of Kittel, when the two impure phases are in equilibrium, the derivatives of the free energy per particle with respect to the impurity concentrations of the two phases are equal:

$$\begin{aligned}\frac{\partial f_s}{\partial x_s} &= \frac{\partial f_l}{\partial x_l} \\ \implies f'_s(0) - \tau(1 - \ln x_s) + \tau &= f'_l(0) - \tau(1 - \ln x_l) + \tau \\ \implies \frac{f'_l(0) - f'_s(0)}{\tau} &= \ln(x_s/x_l) \\ \implies k \equiv x_s/x_l &= e^{-(f'_s(0) - f'_l(0))/\tau}.\end{aligned}$$

Plugging in $f'_s(0) - f'_l(0) = 1 \text{ eV}$ and $T = 1000 \text{ K}$ gives

$$\frac{f'_s(0) - f'_l(0)}{\tau} = \frac{(1 \text{ eV})(1.60 \times 10^{-19} \text{ J})}{(1.38 \times 10^{-23} \text{ J/K})(1000 \text{ K})} \approx 11.6$$

and so

$$k \approx e^{-11.6} \sim 9 \times 10^{-6}.$$

Problem 6: Vapor Pressure

(a) At equilibrium, the chemical potential of the solution (μ_s) must be equal to that of its vapor (μ_v): $\mu_s(\tau, p) = \mu_v(\tau, p)$. As we saw in lecture, the chemical potential of a solution with a concentration x of impurities is related to the chemical potential of the pure liquid (μ_l) by

$$\mu_s(\tau, p) = \mu_l(\tau, p) - x\tau. \quad (12)$$

Now to find how the vapor pressure varies with x , we can expand both chemical potentials for small changes in pressure about the vapor pressure of the pure solution, p_0 . To do this, recall from lecture or use the methods of problem 1a to convince yourself that

$$\left(\frac{\partial \mu}{\partial p}\right)_\tau = \frac{V}{N} = v \quad (13)$$

for both the liquid and the vapor, where $v \equiv \frac{V}{N}$ is the volume per particle. Then the chemical potentials of the liquid and vapor can be written as:

$$\begin{aligned} \mu_l(\tau, p) &= \mu_l(\tau, p_0) + (p - p_0)v_l \\ \mu_v(\tau, p) &= \mu_v(\tau, p_0) + (p - p_0)v_v \end{aligned}$$

and using (12) we can write the chemical potential of the solution as

$$\mu_s(\tau, p) = \mu_l(\tau, p_0) + (p - p_0)v_l - x\tau. \quad (14)$$

Setting this equal to $\mu_v(\tau, p)$ and noting that by the definition of the vapor pressure p_0 we have $\mu_l(\tau, p_0) = \mu_v(\tau, p_0)$, we obtain

$$(p - p_0)(v_v - v_l) = -x\tau. \quad (15)$$

Noting that $v_v \gg v_l$ and using the ideal gas law $\tau/v = p \approx p_0$ we get

$$p - p_0 = -xp_0 \quad (16)$$

$$\implies p = p_0(1 - x). \quad (17)$$

(b) From lecture we know that the increase in boiling point temperature due to the solute is

$$\Delta\tau_{\text{solute}} = \frac{x\tau^2}{l} \quad (18)$$

where $x = N_A/N_B$ is the fractional concentration of the solute and l is the latent heat per particle. Now, the presence of the solute also reduces the vapor pressure by the amount (16), which by Clausius-Clapeyron (CC) should *decrease* the boiling temperature. Clausius-Clapeyron says

$$\frac{\partial p}{\partial \tau} = \frac{l}{\tau \Delta v} \quad (19)$$

where $\Delta v = v_g - v_l \approx v_g$ is the change in volume per particle. For small changes in p and τ we can write this as

$$\Delta\tau_{\text{CC}} = \frac{\tau \Delta v}{l} \Delta p = \frac{\tau v_g}{l} (-xp) = -\frac{x\tau^2}{l} \quad (20)$$

where we've used the ideal gas law in the last step and approximated $p \approx p_0$ where permissible. Inspection shows that (18) is the opposite of (20), and so the two changes in the boiling temperature cancel and it remains constant.