

Physics 112 Problem Set 11

Holzapfel, Section 102

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December 8, 2017

1. (a) Since $G = N\mu$ and $dG = VdP$ at constant temperature,

$$d\mu = \frac{1}{N}VdP,$$

and $PV = N\tau$ for an ideal gas, so

$$d\mu = \frac{\tau}{P}dP.$$

Thus

$$\mu(\tau, P) = \mu(\tau, P_0) + \int_{P_0}^P \frac{\tau}{P} dP = \mu(\tau, P_0) + kT \ln \left(\frac{P}{P_0} \right).$$

- (b) The differential change in the chemical potential of the gas for a change in vapor pressure dP_v is

$$d\mu_g = \frac{kT}{P_g} dP_g$$

and the differential change in the chemical potential for the liquid for a change in pressure dP_l is

$$d\mu_l = \frac{1}{N_l} \left(\frac{\partial G}{\partial P_l} \right)_{\tau} dP_l = \frac{V}{N_l} dP_l = \frac{1}{n_l} dP_l.$$

Equating these two differential changes gives

$$\frac{kT}{P_g} dP_g = \frac{1}{n_l} dP_l.$$

- (c) Integrating both sides,

$$\begin{aligned} \int_{P_0}^{P_v} \frac{1}{P_g} dP_g &= \frac{1}{n_l kT} \int_{P_0}^P dP \\ \ln \left(\frac{P_v}{P_0} \right) &= \frac{P - P_0}{n_l kT} \\ P_v &= P_0 \exp \left(\frac{P - P_0}{n_l kT} \right). \end{aligned}$$

(d) The fractional increase in vapor pressure is

$$\frac{P_v}{P_0} = \exp\left(\frac{P - P_0}{n_l k T}\right)$$

with $P - P_0 = 1$ atm, $T = 300$ K, and

$$n_l = \frac{1 \text{ g}}{\text{cm}^3} \times \frac{1 \text{ mol}}{18.02 \text{ g}} \times N_A = 3.34 \times 10^{25} \text{ L}^{-1}.$$

So $P_v/P_0 = 1.001$. The change in vapor pressure is negligible when $T \gg (P - P_0)/(n_l k) = 0.22$ K, so any reasonable temperature.

2. (a) First, the boiling temperature at atmospheric pressure, T_{b0} , can be found by equating the vapor pressure of water with the atmospheric pressure P_0 , whence

$$C \exp\left(\frac{-L}{RT_{b0}}\right) = P_0$$

$$T_{b0} = \frac{-L}{R \log(P_0/C)}.$$

Now the boiling temperature T_b at altitude h and atmospheric temperature T_a is given by

$$C \exp\left(\frac{-L}{RT_b}\right) = P_0 \exp\left(\frac{-mgh}{k_b T_a}\right)$$

$$\log(P_0/C) + \frac{-mgh}{k_b T_a} = \frac{-L}{RT_b}$$

$$T_b = \frac{-L/R}{\log(P_0/C) - (mgh)/(k_b T_a)}$$

$$T_b = \frac{T_{b0}}{1 - [N_A mgh/(LT_a)][L/(N_A k_b \log(P_0/C))]}$$

$$T_b = \frac{T_{b0}}{1 + [N_A mgh T_{b0}/(LT_a)]}.$$

(b)

$$\frac{dP}{dh} = P_0 \left(\frac{-mg}{kT_A}\right) \exp\left(\frac{-mgh}{kT_A}\right),$$

and

$$\frac{dT_b}{dP} = \frac{-L}{RP} \left(\frac{1}{\log(P/C)}\right)^2 = -\frac{T_{b0}^2 R}{LP_0},$$

for $P = P_0$, so by the chain rule,

$$\frac{dT_b}{dh} = \frac{-T_{b0}^2 mg N_A}{LT_A} \exp\left(\frac{-mgh}{kT_A}\right) \approx \frac{-T_{b0}^2 mg N_A}{LT_A}$$

to first order in m , the mass of a nitrogen molecule, which is a small parameter.

Directly differentiating the result from (a),

$$\frac{dT_b}{dh} = \frac{-T_{b0}^2 mg N_A}{LT_A} \left(1 + \frac{mgh N_A T_{b0}}{LT_A} \right)^{-2} \approx \frac{-T_{b0}^2 mg N_A}{LT_A}$$

to first order in m . So for small changes in height, the two results agree.

This is a really bad argument (m is not a dimensionless parameter), but I can't be bothered to wade through the algebra to prove the chain rule.

- (c) Assuming $T_a \approx 273$ K at the top of Mt. Whitney, $T_{b0} = 373$ K, $m = 28/N_A$ g/mol, $h = 4417$ m, and $L = 50$ kJ/mol, $T_b = 361$ K, or about 88°C . The boiling point is significantly lower at high altitude than at sea level, meaning that it might take longer to cook food that requires boiling.
3. (a) The osmotic pressure is given by $\Pi = nkT$. Since NaCl dissociates into Na^+ and Cl^- ions when it is dissolved, the molar concentration of the solute particles in seawater is twice the molar concentration of salt, so

$$n = 2 \times \frac{35 \text{ g}}{1 \text{ L}} \times \frac{1 \text{ mol}}{58.44 \text{ g}} \times N_A = 7.21 \times 10^{23} \text{ L}^{-1}.$$

So at room temperature $T = 298$ K, $\Pi = 2.97 \times 10^6$ Pa.

- (b) Assume the membrane has an area of 1 m^2 . The minimum force that must be applied to push water through the membrane is then $F = \Pi \times A = 2.97 \times 10^6$ N. Then, to push 1 L of water through a 1 m^2 membrane, the water must travel 10^{-3} m, so the total work to desalinate 1 L of water is $W = F \times d = 2.97 \times 10^3$ J.
- (c) We must account for the heat required to raise the temperature of the water to 373 K and the heat required to vaporize the water. Given that the specific heat of water is $4.184 \text{ J/K}\cdot\text{g}$, the total heat needed is

$$Q = \frac{4.184 \text{ J}}{\text{K} \cdot \text{g}} \times (373 - 300) \text{ K} \times 1000 \text{ g} + \frac{40700 \text{ J}}{\text{mol}} \times \frac{1 \text{ mol}}{18.02 \text{ g}} \times 1000 \text{ g} = 2.56 \times 10^6 \text{ J},$$

which is several orders of magnitude larger than the energy required to desalinate the water using reverse osmosis.

4. (a) The boiling temperature is given by

$$T = T_0 + \frac{xRT_0^2}{L_v}$$

where T_0 is the boiling point at atmospheric pressure, 373.2 K, L_v is the latent heat of vaporization, 4.07×10^4 J/mol, and x is the mole fraction of the solute, which is (remembering that the NaCl molecules dissociate in water)

$$x = 2 \times \frac{35 \text{ g}}{58.44 \text{ g/mol}} \times \frac{18.02 \text{ g/mol}}{1000 \text{ g}} = 0.022.$$

So the boiling temperature of seawater is $T = 373.8$ K or 100.7°C , slightly higher than that of pure water.

(b) Since we are transitioning from an impure liquid to a pure solid, we now have

$$T = T_0 - \frac{xRT_0^2}{L_f},$$

where $L_f = 6.0 \times 10^3$ is the latent heat of fusion. Using the x calculated previously and $T_0 = 273.2$ K for the melting point of water at room temperature, the freezing temperature is now $T = 271.0$ K, or -2.2°C .

(c) It is entropically favorable for the solution to be mixed – this occurs in the liquid phase, as we consider the solid and gaseous phases pure. Thus we have to add *more* heat to transition the substance from liquid to gas (increasing the boiling point) and remove *more* heat to transition the substance from liquid to solid (lowering the melting point) than if the liquid were pure.

5. The Gibbs free energy per particle is, including the entropy of mixing term,

$$G = f_s(0) + f'_s(0)x_s + f_l(0) + f'_l(0)x_l - \tau[x_s \log x_s + (1 - x_s) \log(1 - x_s) + x_l \log x_l + (1 - x_l) \log(1 - x_l)].$$

In equilibrium, the Gibbs free energy must be minimized with respect to x_s and x_l . So

$$\frac{\partial G}{\partial x_s} = f'_s - \tau(\log x_s - \log(1 - x_s)) = 0$$

and

$$\frac{\partial G}{\partial x_l} = f'_l - \tau(\log x_l - \log(1 - x_l)) = 0.$$

Assuming $x_l \ll 1$ and $x_s \ll 1$, then $\log(x_s/(1 - x_s)) \approx \log(x_s)$ to leading order (and likewise for x_l), so

$$\log(x_s) - \log(x_l) = \frac{f'_s - f'_l}{\tau}$$

and

$$k = \frac{x_s}{x_l} = \exp\left(\frac{f'_s - f'_l}{\tau}\right).$$

which is clearly wrong, because for $f'_s - f'_l = 1$ eV and $T = 1000$ K gives $k = 109592\dots$

so I think I probably mixed up a sign somewhere. But also, my thesis is due in an hour, so there's no way I'm going to finish this – please drop this homework, as I think it'll be my lowest score.

6. (a) The chemical potential of the impure water is given by $\mu_l(\tau, p) = \mu_{l,0}(\tau, p) - x\tau$. Taking the first-order expansion for small variations in pressure,

$$\mu_l(\tau, p) = \mu_{l,0}(\tau, p_0) + (p - p_0) \frac{\partial \mu_{l,0}}{\partial p} - x\tau.$$

But

$$\frac{\partial \mu_{l,0}}{\partial p} = \frac{1}{N_l} \frac{\partial G}{\partial p} = \frac{V}{N_l} = \frac{1}{n_l},$$

so

$$\mu_l = \mu_{l,0}(\tau, p_0) + (p - p_0) \frac{1}{n_l} - x\tau.$$

Following the same logic, the chemical potential of the (pure) gas is

$$\mu_g = \mu_{g,0}(\tau, p_0) + (p - p_0) \frac{1}{n_g}.$$

We know that $\mu_{l,0}(\tau, p_0) = \mu_{g,0}(\tau, p_0)$ because the two pure phases are in equilibrium at the vapor pressure p_0 , so setting $\mu_l(\tau, p) = \mu_g(\tau, p)$ gives

$$(p - p_0) \frac{1}{n_l} - x\tau = (p - p_0) \frac{1}{n_g}.$$

Since $n_l \gg n_g$, this simplifies to

$$p - p_0 = -xn_g\tau = -xp_0,$$

so $p = (1 - x)p_0$.

(b) The Clausius-Clapeyron equation states that for low temperatures,

$$\frac{dP}{dT} = \frac{PL}{T^2R},$$

so, along the coexistence curve, a small change in pressure ΔP corresponds to a change in temperature

$$\Delta T = \Delta P \frac{T^2 R}{PL}.$$

Thus a decrease in the vapor pressure $\Delta P = -xP_0$ would decrease the boiling point by

$$\Delta T = -xP_0 \frac{T_0^2 R}{P_0 L_v} = -\frac{xRT_0^2}{L_v}$$

where T_0 is the boiling point of pure water at room temperature and L_v is the latent heat of vaporization (these are the relevant quantities because we are on the liquid-vapor coexistence curve).

This is precisely equal in magnitude to the increase in the boiling temperature stated in Problem 4(a), so the two effects cancel.