

Homework 11 Solutions

Question 1

Kittel+Kromer, Chpater 10, Problem 1

a) We know the Helmholtz free energy of the vdW gas:

$$F_{vdW} = -N\tau \left\{ \log \left(\frac{n_Q(V - Nb)}{N} \right) + 1 \right\} - \frac{N^2 a}{V} \quad (1)$$

The entropy can be found from

$$\sigma = - \frac{\partial F}{\partial \tau} \Big|_V \quad (2)$$

$$= N \left\{ \log \left(\frac{n_Q(V - Nb)}{N} \right) + 1 \right\} + N\tau \left\{ \frac{N}{n_Q(V - Nb)} \frac{(V - Nb)}{N} \frac{dn_Q}{d\tau} \right\} \quad (3)$$

Using $n_Q = \left(\frac{m\tau}{2\pi\hbar^2} \right)^{3/2}$ we obtain

$$\sigma = N \left\{ \log \left(\frac{n_Q(V - Nb)}{N} \right) + \frac{5}{2} \right\} \quad (4)$$

b) The energy U can be obtained from F by differentiation w.r.t. τ or simply using $F = U - \tau\sigma$:

$$U = F + \tau\sigma \quad (5)$$

$$= -N\tau \left\{ \log \left(\frac{n_Q(V - Nb)}{N} \right) + 1 \right\} - \frac{N^2 a}{V} + \tau \times N \left\{ \log \left(\frac{n_Q(V - Nb)}{N} \right) + \frac{5}{2} \right\} \quad (6)$$

$$= \frac{3}{2}N\tau - \frac{N^2 a}{V} \quad (7)$$

which is the ideal gas energy plus the vdW correction for attractive interactions.

Question 2

Kittel+Kromer, Chpater 10, Problem 2 We will use the C-C equation

$$\frac{dp}{dT} = \frac{L}{T\Delta V} \quad (8)$$

together with the ideal gas law $\Delta V \approx \tau/p$. Here we have an approximate equality since the volume of the liquid phase is not exactly zero, but it is negligible compared to the volume of the gas at normal pressures.

$$\frac{dp}{dT} = \frac{L}{T^2 k_B} p \quad (9)$$

Also note that in the C-C equation L is latent heat per particle, whereas we are given the latent heat per gram. To do the conversion it is convenient to multiply the numerator and denominator by Avogadro's number N_A :

$$\frac{dP}{dT} = \frac{LN_A}{N_A k_B T^2} p \quad (10)$$

where LN_A is the latent heat per mole of H_2O , which is $2260 J/g \times 18 g/mole = 40,680 J/mole$ and $N_A k_B$ is the universal gas constant $R = 8.314 J/mole K$. Hence

$$\frac{dp}{dT} = 0.035 \frac{atm}{K} \quad (11)$$

$$\frac{dT}{dp} = 28.4 \frac{K}{atm} \quad (12)$$

Question 3

Kittel+Kromer, Chapter 10, Problem 3 The data given is summarized in a plot below.

FIG. 1: Summary of data given in the problem

The coexistence line is described by the C-C equation

$$\frac{dp}{dT} = \frac{L}{T \Delta V} \approx \frac{L}{k_B T^2} p = \frac{LN_A}{RT^2} p \quad (13)$$

where we have proceeded as in question 2, above. The latent heat of vaporization is:

$$LN_A = \frac{RT^2}{p} \frac{dp}{dT} \quad (14)$$

At $T = -1^\circ C$ we estimate the pressure as $P \approx \frac{4.58+3.88}{2} mmHg = 4.23 mmHg$. The slope of the coexistence line is

$$\frac{dp}{dT} \approx \frac{\Delta p}{\Delta T} = \frac{4.58 mmHg - 3.88 mmHg}{2 K} = 0.35 \frac{mmHg}{K} \quad (15)$$

Thus the latent heat of vaporization is

$$LN_A = \frac{8.31 \frac{J}{mole K} (272 K)^2}{4.23 mmHg} \frac{0.35 mmHg}{K} = 5.09 \times 10^4 \frac{J}{mole} \quad (16)$$

Question 4

Kittel+Kromer, Chapter 10, Problem 4

a) The atoms in the solid are 3D harmonic oscillators with a ground state energy of $-\varepsilon_0$

$$\varepsilon_s = (n_x + n_y + n_z)\hbar\omega - \varepsilon_0 \quad (17)$$

with $n_x, n_y, n_z = 1, 2, \dots$. The partition function for a single atom in the solid is

$$Z_s = \sum_{n_x} \sum_{n_y} \sum_{n_z} e^{-[(n_x + n_y + n_z)\hbar\omega - \varepsilon_0]/\tau} \quad (18)$$

$$= e^{\varepsilon_0/\tau} \left(\sum_n e^{-n\hbar\omega/\tau} \right)^3 \quad (19)$$

The summation is the geometric sum which we have already seen before and gives $\frac{1}{1 - e^{-\hbar\omega/\tau}}$. Hence the partition function becomes:

$$Z_s = \frac{e^{\varepsilon_0/\tau}}{(1 - e^{-\hbar\omega/\tau})^3} \quad (20)$$

Now proceed to calculate the activity of the solid as on page 286 of K+K:

$$\lambda_s = e^{-\log Z_s} = \frac{1}{Z_s} = e^{-\varepsilon_0/\tau} (1 - e^{-\hbar\omega/\tau})^3 \quad (21)$$

We use the ideal gas approximation to describe the gas phase and find

$$\lambda_g = \frac{n}{n_Q} = \frac{p}{\tau n_Q} = \frac{p}{\tau} \left(\frac{2\pi\hbar^2}{M\tau} \right)^{3/2} \quad (22)$$

which is Eq. (10.30). If the solid and vapor are in equilibrium, then they share the same chemical potential, temperature and activity:

$$\lambda_g = \lambda_s \quad (23)$$

$$e^{\mu_g/\tau} = e^{\mu_s/\tau} \quad (24)$$

$$\frac{p}{\tau} \left(\frac{2\pi\hbar^2}{M\tau} \right)^{3/2} = e^{-\varepsilon_0/\tau} (1 - e^{-\hbar\omega/\tau})^3 \quad (25)$$

so

$$p = \tau n_Q e^{-\varepsilon_0/\tau} (1 - e^{-\hbar\omega/\tau})^3 \quad (26)$$

This is the vapor pressure over the solid. Now consider the high temperature limit $\tau \gg \hbar\omega$ and do an expansion in terms of the small parameter $\hbar\omega/\tau$:

$$1 - e^{-\hbar\omega/\tau} \approx 1 - \left(1 - \frac{\hbar\omega}{\tau} \dots \right) = \frac{\hbar\omega}{\tau} \quad (27)$$

So the pressure becomes in this limit:

$$p \approx \tau n_Q e^{-\varepsilon_0/\tau} \left(\frac{\hbar\omega}{\tau} \right)^3 \quad (28)$$

$$= \frac{\omega^3}{\tau^2} \left(\frac{M\tau}{2\pi} \right)^{3/2} e^{-\varepsilon_0/\tau} \quad (29)$$

$$= \frac{\omega^3}{\sqrt{\tau}} \left(\frac{M}{2\pi} \right)^{3/2} e^{-\varepsilon_0/\tau} \quad (30)$$

b) The latent heat can be found from the C-C equation with the ideal gas approximation:

$$\frac{d}{d\tau} \log p = \frac{1}{p} \frac{dp}{d\tau} = \frac{L}{\tau^2} \quad (31)$$

First form $\log p$ from the result for part a).

$$\log p = -\frac{1}{2} \log \tau - \frac{\varepsilon_0}{\tau} + \text{const.} \quad (32)$$

Take the τ derivative

$$\frac{d}{d\tau} \log p = -\frac{1}{2\tau} + \frac{\varepsilon_0}{\tau^2} \quad (33)$$

$$= \frac{1}{\tau^2} \left(\varepsilon_0 - \frac{\tau}{2} \right) \quad (34)$$

$$= \frac{L}{\tau^2} \quad \text{by Eq. (10.18)} \quad (35)$$

Hence the latent heat per atom is

$$L = \varepsilon_0 - \frac{\tau}{2} \quad (36)$$