

Oblig 3 - Vapour Pressure

FYS2160 at University of Oslo

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a)

For one atom A in a crystal, the partition function (sum over all energy microstates i) would be given as:

$$Z = \sum_i e^{-\epsilon_i/k_B T}$$

or alternatively (and maybe more commonly)

$$Z = \sum_i e^{-\beta \epsilon_i}$$

where $\beta = \frac{1}{k_B T}$

however, as our atom A is bound, we instead find (because it only has one microstate):

$$Z = e^{\beta \epsilon_A} \tag{1}$$

b)

First, we must find the sum of all partition functions:

$$Z_1^{N_A} = \sum_{i=1}^{N_A} e^{\beta \epsilon_A}$$

or alternatively, in this special case where there is only one energy microstate:

$$Z_1^{N_A} = N_A e^{\beta \epsilon_A}$$

We can then find the total partition function for a system of N_A atoms as:

$$Z_{N_A} = \frac{1}{N_A!} Z_1^{N_A} \tag{2}$$

c)

Remind yourself that the Helmholtz free energy is given as:

$$F = U - TS$$

where U is the total energy of our system and S is the entropy. It follows then that we can express this as:

$$F = U - TS = -k_B T \ln Z_{N_A} \quad (3)$$

d)

We know that the pressure P and temperature T are constant. Therefore, we find that:

$$\mu = \left(\frac{\delta G}{\delta N_A} \right)_{T,P}$$

$$G_A = N_A \mu$$

Or alternatively (using P , V_A and T as asked):

$$G = F + PV_A$$

$$G = -k_B T \ln Z_{N_A} + PV_A \quad (4)$$

e)

The chemical potential can be expressed as:

$$\mu(T, P) = \frac{G}{N_A} = \mu_A = \left(\frac{\delta G}{\delta N_A} \right)_{T,P}$$

using then G from Equation [4] and the free energy:

$$F = -k_B T \ln Z_N = -k_B T \ln Z$$

where Z is from Equation [1], gives (the second term becomes zero because $N = N_A$):

$$\mu(T, P) = -\epsilon_A - k_B T(0) + P v_A$$

$$\mu(T, P) = -\epsilon_A + P v_A \quad (5)$$

f)

When dealing with vapour pressure, we're looking at equilibrium between the solid and gas, and as such, the chemical potential of our gas must be equal to the chemical potential of our solid, which means:

$$\mu_A = -\epsilon_A = \mu = k_B T \ln \frac{n}{n_Q(T)}$$

$$\frac{n}{n_Q(T)} = e^{\frac{-\epsilon_A}{k_B T}}$$

$$n = n_Q(T) e^{-\beta \epsilon_A}$$

We can then rewrite n as $\frac{p_A}{k_B T}$ (because $n = \frac{N}{V}$, giving us the ideal gas law), and we get:

$$p_A(T) = n_Q(T) k_B T e^{-\beta \epsilon_A} \quad (6)$$

g)

S is given as:

$$S = - \left(\frac{\delta F}{\delta T} \right)_V$$

Let us first find F, as it has changed.

Recall that:

$$F = -k_B T \ln Z_N$$

The partition function for our B atoms is:

$$Z_B = e^{\beta \epsilon_B}$$

and A atoms are Equation [1].

We can now express the total partition function, and new Z_N as:

$$Z_N = \binom{N}{N_A} Z_A^{N_A} Z_B^{N_B}$$

The free energy is then:

$$F = -N_A \epsilon_A - N_B \epsilon_B - k_B T ((N_A + N_B) \ln(N_A + N_B) - N_A \ln N_A - N_B \ln N_B)$$

Now, we can either look at this intuitively, given that:

$$F = E - TS$$

then

$$E = -N_A \epsilon_A - N_B \epsilon_B$$

and

$$TS = T k_B ((N_A + N_B) \ln(N_A + N_B) - N_A \ln N_A - N_B \ln N_B)$$

Alternatively, inserting F in $S = - \left(\frac{\delta F}{\delta T} \right)_V$ now gives (confirming our intuition from above):

$$S = k_B ((N_A + N_B) \ln(N_A + N_B) - N_A \ln N_A - N_B \ln N_B)$$

Recall that $N_B \ll N_A$, giving:

$$S = k_B \left(N_B \ln \frac{N_A}{N_B} + N_B \right)$$

which is:

$$S = N_B k_B \left(\ln \frac{N_A}{N_B} + 1 \right) \quad (7)$$

as requested

h)

Recall that the Gibbs free energy is given as:

$$G = F + PV$$

It then follows naturally, using the same F that was used to find Equation [7]:

$$G = F + P(N_A v_A + N_B v_B)$$

or, if we're assuming $v_B \approx 0$:

$$G = F + N_A P v_A \quad (8)$$

i)

This chemical potential can in this case be expressed as:

$$\mu_A = \left(\frac{\delta G}{\delta N_A} \right)_{T,P}$$

We insert, using that $N_B \ll N_A$ and $v_b \approx 0$

$$\mu_A = -\epsilon_A + Pv_A - k_B T \frac{N_B}{N_A}$$

I'm assuming μ_A^0 is μ from Equation [5], which gives:

$$\mu_A = \mu_A^0 - k_B T \frac{N_B}{N_A} \quad (9)$$

j)

Again, we need to look at equilibrium between the chemical potentials on the A-atoms and B-atoms respectively. There is no reason to assume that the chemical potential on B-atoms would be anything other than the "opposite" of μ_A , giving:

$$\mu_B = -\epsilon_B + Pv_B - k_B T \frac{N_A}{N_B}$$

which means:

$$\mu_A = -\epsilon_A + Pv_A - k_B T \frac{N_B}{N_A} = \mu_B = -\epsilon_B + Pv_B - k_B T \frac{N_A}{N_B}$$

Remember that we're assuming here that Pv_A is very small in comparison to ϵ_A , giving:

$$-\epsilon_A - k_B T \frac{N_B}{N_A} = -\epsilon_B - k_B T \frac{N_A}{N_B}$$

Using the same principle as before, in regards to the ideal gas law (dividing both sides by v_A to find P_A):

$$-\frac{\epsilon_A}{v_A} - k_B T \frac{N_B}{N_A v_A} = -\frac{\epsilon_B}{v_A} - \frac{P_A}{N_B}$$

Reverse the signs so that everything is positive, and isolate P_A :

$$P_A(T) = \frac{N_B}{v_A} \left[\epsilon_A + k_B T \frac{N_B}{N_A} - \epsilon_B \right] \quad (10)$$

k)

There are some things to comment on here, perhaps most importantly that our vapour-pressure function $P_A(T)$ is linear, as opposed to the characteristic exponential growth of a normal vapour-pressure function. For example, our vapour pressure from Equation [6] is (as expected) exponential. However, also as expected, the vapour pressure increases (almost) linearly with N_B , linearly if we still assume that $N_B \ll N_A$.

I do not know whether these restrictions are a fault of the model and the assumptions we made along the way, or if I have made some wrong assumptions on my end and/or calculations along the way.

I would assume it's the latter, but I am not able to track down whatever is causing it.