

Oblig 3 - FYS2160

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a)

Using the canonical ensemble (N,V,T) Boltzmann factor

$$e^{-E\beta}$$

where $\beta = \frac{1}{kT}$ we can write the partition function as the normalization factor as the sum of all the energy states, in this case is only one

$$Z = \sum_{\epsilon_i} e^{\epsilon_i/(kT)} = e^{\epsilon_A/(kT)} \quad (1)$$

b)

The atoms are distinguishable because they each have specific positions in the lattice unique to them. For distinguishable atoms we can write the total partition function as the product of each atom's partition function, for a system of N_A A atoms with identical energy $-\epsilon_A$ we then get

$$\begin{aligned} Z &= \prod_{i=1}^{N_A} Z_i \\ &= \left(e^{\epsilon_A/(kT)} \right)^{N_A} \\ &= e^{N_A \epsilon_A/(kT)} \end{aligned} \quad (2)$$

c)

Helmholtz free energy is defined as

$$F = U - TS$$

but we can write it as the following and use (1):

$$\begin{aligned} F &= -kT \ln Z \\ &= -kT \ln \left(e^{N_A \epsilon_A/(kT)} \right) \\ &= -kT N_A \epsilon_A/(kT) \\ &= -N_A \epsilon_A \end{aligned} \quad (3)$$

d)

The Gibbs free energy is defined as

$$G = U - TS + pV$$

which gives us

$$\begin{aligned} G &= F + pV \\ &= -N_A \epsilon_A + pN_A v_A \end{aligned} \quad (4)$$

where I used $V = N_A v_A$.

e)

We use the definition

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{p,T}$$

and derive from (4):

$$\begin{aligned} \mu_A(p, T) &= \left(\frac{\partial G}{\partial N_A} \right)_{p,T} \\ &= -\epsilon_A + p v_a \\ &\simeq -\epsilon_A \end{aligned} \quad (5)$$

with $p v_a \ll \epsilon_A$.

f)

We set our expression for the solid's μ_A equal to the gas' μ provided as equation (1) of the oblig:

$$\mu = \mu_A$$

$$kT \ln \frac{N/V}{n_Q(T)} = -\epsilon_A$$

here we use the ideal gas law $PV = NkT \Rightarrow N/V = P/(kT)$:

$$kT \ln \frac{P/(kT)}{n_Q(T)} = -\epsilon_A$$

$$\ln \frac{P/(kT)}{n_Q(T)} = -\frac{\epsilon_A}{kT}$$

$$\frac{P/(kT)}{n_Q(T)} = \exp\left(-\frac{\epsilon_A}{kT}\right)$$

$$\Rightarrow p_A(T) = P = kT n_Q(T) \exp\left(-\frac{\epsilon_A}{kT}\right) \quad (6)$$

where $n_Q(T) = (2\pi mkT/h^2)^{3/2}$.

g)

We use the following expression We use from oblig 2 that

$$\ln \Omega(N, q) \simeq N \left(\ln \frac{q}{N} + 1 \right)$$

where q is the energy divided into N units. Here we can use the same expression where we split N_B atoms over N_A units and get

$$\ln \Omega \simeq N_B \left(\ln \frac{N_A}{N_B} + 1 \right)$$

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

h)

Now we put in the expression for S and total energy $U = -N_A \epsilon_A - N_B \epsilon_B$ and $V \simeq v_a$:

$$G = (-N_A \epsilon_A - N_B \epsilon_B) - T N_B k \left(\ln \frac{N_A}{N_B} + 1 \right) + p v_A$$

now we use $p v_A \ll \epsilon_A$ and get

$$G \simeq -N_A \epsilon_A - N_B \epsilon_B - N_B k T \left(\ln \frac{N_A}{N_B} + 1 \right) \quad (8)$$

i)

We use the definition

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

and derive from (8):

$$\mu_A = \frac{\partial G}{\partial N_A}$$

$$= -\epsilon_A - kT \frac{N_B}{N_A}$$

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

where $\mu_A^0 = -\epsilon_A$ from (5) is the chemical potential without any B atoms.

j)

This will become almost identical to (6) but we just have another term in μ_A during the derivation. Therefore we can just add the second term inside the exponential and get

$$p_A(T) = kT n_Q(T) \exp \left(\frac{-\epsilon_A - kT \frac{N_B}{N_A}}{kT} \right)$$

$$= kT n_Q(T) \exp \left(\frac{-\epsilon_A}{kT} - \frac{N_B}{N_A} \right) \quad (10)$$

k)

This means the vapour pressure has decreased after mixing in the B atoms and decreases when N_B/N_A increases.