LULEÅ TEKNISKA UNIVERSITET
Avdelningen för materialvetenskap

Exam in: STATISTICAL PHYSICS AND THERMODYNAMICS 2015-03-27 (F7035T)
Suggested solutions

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1. Separation of phases is treated in the course book chapter 11. A couple of important topics of a good solution are: The treatment of 'entropy of mixing' $\sigma_M = -N[(1-x)\ln(1-x)+x\ln(x)]$. The free energy $f = u - \tau\sigma$ (per atom). The construction of a graph of $\frac{\sigma_M}{N}$ vs x. Figure I of the problem gives a free energy that gives rise to a separation of phases below a certain temperature into two phases of different mixing x. Figure II does not support any phase separation of the mixture.

2. Here Clausius–Claypeyrons equation will be used : $\frac{dp}{dT} = \frac{q}{T\Delta v}$ as we follow the phase boundary. $\frac{dp}{dT} = \frac{\Delta p}{\Delta T} = -\frac{3.689 \cdot 10^9}{T}$ ($\Delta v = v_{\text{liquid}} - v_{\text{is}} = \frac{1}{999.8} - \frac{1}{916.8} = -9.0550 \cdot 10^{-5}$ m^3/kg, $q = 334 \cdot 10^3$ J/kg). This gives for small changes of temperature: $\Delta T = -\frac{T\Delta p}{3.689 \cdot 10^9} = -0.0666 \approx -0.07$K, ie a lowering of the freezing point by 0.07K.

3. As only the difference is of interest we can put the energy of the ground state to zero and the excited state to ϵ. The partition sum becomes: $Z = 1 + 2e^{-\epsilon/\tau}$ and hence the energy will be $U =<\epsilon>= \frac{0+2\epsilon e^{-\epsilon/\tau}}{1+2e^{-\epsilon/\tau}} = \frac{2\epsilon}{2+e^{\epsilon/\tau}} = \frac{2\epsilon}{2+e^{\epsilon/k_BT}}$ an alternative rout is to take the derivative of Z which gives $U = \tau^2 \frac{\partial \ln Z}{\partial \tau} = \tau^2 \frac{1}{Z} 2e^{-\epsilon/\tau} \frac{\epsilon}{\tau^2} = \frac{2\epsilon}{2+e^{\epsilon/\tau}} = \frac{2\epsilon}{2+e^{\epsilon/k_BT}}$. Finally we arrive at C_v by a derivative of U with respect to τ $C_v = \frac{\partial U}{\partial \tau} = \frac{2\epsilon^2 e^{\epsilon/\tau}/\tau^2}{(2+e^{\epsilon/\tau})^2}$. This can be written as $\frac{2x^2e^x}{(2+e^x)^2}$ where $x = \epsilon/\tau$. To find the maximum take the derivative with respect to x. $\frac{(2x+x^2)e^x}{3+e^x)^2} - \frac{2x^2e^{2x}}{(3+e^x)^3} = 0$ which gives the condition $(x-2)(e^x-2) = 8$. This may be solved graphically or by a pocket calculator. The solution is $x \approx 2.655$ ie. $\epsilon = x\ \tau = x\ k_B\ T = 2.655 \cdot 1.3807 \cdot 10^{-23} \cdot 330 = 1.210 \cdot 10^{-20}$ J $= 0.0756$ eV $= 75.6$ meV.

4. a) The partition sum is given by: $Z = \sum_{n_1=0,n_2=0}^{\infty} e^{-(n_1+n_2+1.0)\hbar\omega/k_BT} = \sum_{n=0}^{\infty} g(n)e^{-(n+1.0)\hbar\omega/k_BT}$, where $g(n)$ is the degeneracy of the energy levels and $n = n_1+n_2$. There are two ways to evaluate this sum. One simple and one more elaborate. Only the simple solution is presented here. The sum for Z can be done as a product of two separate independent geometric sums.
$Z = \sum_{n_1=0,n_2=0}^{\infty} e^{-(n_1+n_2+1.0)\hbar\omega/k_BT} = \sum_{n_1=0}^{\infty} e^{-(n_1+0.5)\hbar\omega/k_BT} \cdot \sum_{n_2=0}^{\infty} e^{-(n_2+0.5)\hbar\omega/k_BT} = \left(\sum_{n=0}^{\infty} e^{-(n+0.5)\hbar\omega/k_BT}\right)^2 = e^{-\hbar\omega/k_BT}\left(\sum_{n=0}^{\infty} e^{-n\hbar\omega/k_BT}\right)^2 = e^{-\hbar\omega/k_BT}\left(\frac{1}{1-e^{-\hbar\omega/k_BT}}\right)^2 =$ and we arrive at the following for the partition function Z:

$$Z = \left(\frac{1}{e^{+\hbar\omega/2k_BT} - e^{-\hbar\omega/2k_BT}}\right)^2 = \text{ or } = e^{-\hbar\omega/k_BT}\left(\frac{1}{1-e^{-\hbar\omega/k_BT}}\right)^2.$$

b) There is one state of the lower energy and two states with the next higher energy. The probability to find the oscillator in a state of energy is proportional to the Boltzmann factor, we arrive at the following equation. $1e^{-1{,}0\hbar\omega/k_BT} = 2e^{-2{,}0\hbar\omega/k_BT}$ and $e^{1\hbar\omega/k_BT} = 2$ which evaluates to $T = \frac{1\hbar\omega}{k_B \ln 2}$ or if you prefer τ, $\tau = \frac{1\hbar\omega}{\ln 2}$, which is equally correct.

c) The partition sum at this specific temperature is given by: $(k_BT = \tau = \frac{1\hbar\omega}{\ln 2})$ we arrive at the following

$$Z = \left(\frac{1}{e^{+\frac{\ln 2}{2}} - e^{-\frac{\ln 2}{2}}}\right)^2 = \left(\frac{1}{\sqrt{2} - \frac{1}{\sqrt{2}}}\right)^2$$

We continue with the calculation of the probability: (we may choose any of the two energies as their probabilities will be equal at the temperature in question: $(1e^{-1{,}0\hbar\omega/k_BT} = 2e^{-2{,}0\hbar\omega/k_BT})$

$$P = e^{-\hbar\omega/k_BT} / \left(\frac{1}{\sqrt{2} - \frac{1}{\sqrt{2}}}\right)^2 = 2^{-1}\left(\sqrt{2} - \frac{1}{\sqrt{2}}\right)^2 = \left(\frac{1}{\sqrt{2}}\right)^2\left(\sqrt{2} - \frac{1}{\sqrt{2}}\right)^2 =$$

$$\left(1 - \frac{1}{2}\right)^2 = \frac{1}{4} = 0.25$$

The probability to be in a state of one of these energys is $P = \frac{1}{4} = 0.25$

5. There are five different states of hemoglobin depending on the number of bound oxygen molecules 0, 1, 2, 3, or 4. For each of these the number of different ways to attach the oxygen molecules are 1, 4, 6, 4 and 1. The chemical activity of O_2 is $\lambda = e^{\mu/\tau}$, where ϵ is the energy of bound O_2. The Grand partition sum is $Z = 1 + 4\lambda e^{-\epsilon/\tau} + 6\lambda^2 e^{-2\epsilon/\tau} + 4\lambda^3 e^{-3\epsilon/\tau} + \lambda^4 e^{-4\epsilon/\tau}$. The probability for one O_2 molecule is $P(1) = \frac{4\lambda e^{-\epsilon/\tau}}{Z}$ and to have four O_2 molecules is $P(4) = \frac{\lambda^4 e^{-4\epsilon/\tau}}{Z}$.

   A graph of $P(1)$ vs λ will start at zero and pass a maximum value and approach zero again as λ increases.

   A graph of $P(4)$ vs λ will start at zero and start to increase after the maxima of $P(1)$, $P(2)$ and $P(3)$ have passed to the saturation value 1 as λ increases.