

CH352 Assignment 4. Due: Friday, April 18, 2014

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Q1 Harmonic Oscillator Thermodynamics:

- (i) Compute the canonical ensemble partition function, $q = \sum_{n=0}^{\infty} e^{-\beta \epsilon_n}$ where $\beta = 1/k_b T$, for a harmonic oscillator, call it q_{HO}
- (ii) Compute the internal energy, U , and constant volume heat capacity C_V of a harmonic oscillator. (iii) Use your result from (i) to compute the Helmholtz free energy of a harmonic oscillator, $A_{HO}(T, V, N)$. Give your answer in simplified form.
- (iv) Compute the entropy of a harmonic oscillator S_{HO} . (Hint: it might make life easier to use the chain rule and the fact that $\frac{d\beta}{dT} = -\frac{1}{k_B T^2}$).

Q2 Consider a gas phase system of N identical independent O atoms, with partition function Q . Suppose the single particle partition function is the product of a translational partition function, q_t , and an electronic partition function, q_e , so

$$q = q_t q_e \tag{1}$$

The nine electronic states of the lowest energy 3P electronic level are split due to spin-orbit coupling. Table 1 lists various characteristics of these states as well as some of the higher energy levels. Data are reported for $T = 300K$, and for convenience energies are given in Kelvin units.

- (a) Use the fact that the internal energy is

$$U = -\frac{1}{Q} \frac{\partial Q}{\partial \beta} \tag{2}$$

$^{2S+1}L_J$	$g = 2J + 1$	$\Delta\epsilon_n/k_B = (\epsilon_n - \epsilon_0)/k_B$	$\beta\Delta\epsilon_n$	$(\beta\Delta\epsilon_n)^2$
3P_2	5	0 K	0	0
3P_1	3	232 K	0.7733	0.5980
3P_0	1	348 K	1.16	1.3456
1D_2	5	22,860 K	76.2	
1S_0	1	48,621 K	162.1	

Table 1: Atomic oxygen electronic energy level characteristics

to show that

$$U = -N \left[\frac{1}{q_t} \frac{\partial q_t}{\partial \beta} + \frac{1}{q_e} \frac{\partial q_e}{\partial \beta} \right] = U_t + U_e \quad (3)$$

(b) Calculate: (i) the translational component of the internal energy U_t , and (ii) the translational component of the constant volume heat capacity

$$C_v^t = \left(\frac{\partial U_t}{\partial T} \right)_{NV} \quad (4)$$

(c) Comment on why we can neglect the contributions from the states 1D_2 and 1S_0 at room temperature and calculate the general expression in this case for: (i) the electronic component of the internal energy U_e , and (ii) make life easier by calculating the electronic heat capacity using the result

$$C_v^e = -k_B \beta^2 \left(\frac{\partial U_e}{\partial \beta} \right)_{NV} \quad (5)$$

(d) You should be able to write your results from (b) and (c) in the form, $C_v = Nk_B \times$ (dimensionless number). Compute these dimensionless numbers for C_v^t and, use the data in Table 1 for $T = 300\text{K}$, to compute the dimensionless number for C_v^e at this temperature. Hence you can get an idea of how big the spin-orbit contribution to the heat capacity of atomic O at room temperature is compared to the translational heat capacity.

Q3 The constant volume heat capacity of a substance can also be written as

$$C_v = T \left(\frac{\partial S}{\partial T} \right)_{VN} \quad (6)$$

Use Maxwell relations to obtain a simple expression for $(\partial C_v / \partial N)_{VT}$ in terms of some second derivative, or curvature quantity. The fact that C_v is extensive means that $(\partial C_v / \partial N)_{VT}$ must be positive. So the curvature result that you derived above tells you what about the quantities involved?

Q4 (a) Write down an expression for the entropy, S , of an ideal gas of N independent, indistinguishable particles in terms of the thermal wavelength Λ and the system volume, V (see Eq.(4) above). Here

$$\Lambda = \left(\frac{h^2}{2\pi m k_B T} \right)^{1/2} \quad (7)$$

(b) Use your expression from (a) to compute the derivative $(\partial \mu / \partial T)_{VN}$.

Q5 Consider a system of N identical molecules with magnetic moments of strength m_0 . Suppose the density of the sample is sufficiently low that the molecules essentially do not interact with one another and they can be regarded as independent. In the presence of a magnetic field \mathbf{B} the molecules have two possible energy states: the lowest energy state in which the magnetic moments align parallel to the field and have energy $E_- = -m_0 B$, and the higher energy state in which the moments align anti-parallel to the field and have energy $E_+ = m_0 B$. Suppose the system is in thermal equilibrium at a temperature T .

(a) (i) Give an expression for the many-body partition function, Q in terms of N , T , m_0 and B , and (ii) use your result to compute the Helmholtz free energy, $A = -k_B T \ln Q$, for this system.

(b) The change in Helmholtz free energy for this system is

$$dA = -SdT + MdB + \mu dN \quad (8)$$

where M is the magnetization of the sample induced by the application of the \mathbf{B} field. Use your expression from (a) (ii) to compute the magnetization M in terms of N , T , m_0 and B and interpret your result in terms of the average magnetization of a single particle.

(c) Explain how you could use your expression for the magnetization in (b) to compute the rate at which the entropy of the sample changes with increasing field strength *i.e.* $(\partial S/\partial B)_{T,N}$

Q6 Thermodynamics of molecular binding to surfaces:

When molecules bind to a surface some of their motions are transformed into different types of motion. For example, instead of translating like gas phase molecules in three dimension, (x, y, z) , molecules in a surface adsorbed phase can translate only in two dimensions (x, y) parallel to the surface, while their motion perpendicular to the surface (the z -direction, say) has been transformed into a vibration of the “bond” holding the molecule to the surface.

Suppose one wall of a cubic box with side length $L=10\text{ cm}$ is coated with a material that can bind helium atoms with a binding energy $E_{bind} = -\epsilon$, where the magnitude of the binding energy per mole is $N_A\epsilon = 100\text{ kJ mol}^{-1}$. The other walls of the container do not bind helium. Once bound on the coated surface, to a good approximation, as discussed above, the particles translate freely over the surface in the $x - y$ plane and vibrate harmonically perpendicular to the surface (z -direction) with a frequency ν_s . Thus the surface vibrational state energies are $E_n = -\epsilon + (n + 1/2)h\nu_s$. For later use we will suppose that the magnitude of the ground state vibrational energy per mole of bound molecules is $N_A(h\nu_s/2) = 20\text{ kJ mol}^{-1}$.

(i) Use the series sum approach to show that the vibrational part of the partition function, $q_s^{(vib)}$ of a molecule bound to the surface with this shifted vibrational energy level spectrum is

$$q_s^{(vib)} = \frac{e^{\beta h\nu_s/2} e^{\beta\epsilon}}{[1 - e^{-\beta h\nu_s}]}$$

(ii) Combine your surface vibrational partition function from (i) with the appropriate expression for the surface translational partition function $q_s^{(trans)}$ to obtain an expression for the total partition function of a surface bound particle. Express your result in terms of the thermal wavelength, $\Lambda = [h^2\beta/(2\pi m)]^{1/2}$, and the box length L . Assume the molecule is always in its non-degenerate electronic ground state, and for 1d translational motion in a region of length L , $q_s^{(trans)} = L/\Lambda$.

(iii) Up to this point you have been exploring molecules in a surface bound phase, now we consider the gas phase. Suppose a molecule has broken its bond to the surface and has entered the gas phase. It thus can translate freely in x , y , and z . Write down the partition function, q_g , of a molecule in the gas phase in the box.

(iv) Suppose there are $N = nN_A$ independent, distinguishable molecules. Use your partition function expressions in (ii) and (iii) to compute the free energy difference, $\Delta A = A_s - A_g$, between having all N molecules adsorbed in the surface phase, and having all molecules desorbed into the gas phase. Simplify your free energy difference expression by recognizing that when $h\nu_s \gg k_B T$, $\exp[-\beta h\nu_s] \ll 1$, and rewrite it as the free energy difference per mole $\Delta A/n$.

(v) The thermal wavelength should appear under a logarithm in the expression you obtained in (iv). As such, to a good approximation, we can ignore the temperature dependence of the thermal wavelength compared to the other temperature dependence in your expression obtained in (iv). Assume the thermal wavelength is approximately constant and equal to its value at $T = 300K$ which, for a helium atom is $\Lambda = 0.5 \times 10^{-10}$ m. Use this approximation, and your expression for $\Delta A/n$ to predict the temperature, T_e , at which the system will undergo an evaporation phase transition, where the surface bound phase first becomes less stable than the gas phase.

Useful information:

You will simplify computations using the gas constant $R = N_A k_B = 8.314 JK^{-1} mol^{-1}$