STATISTICAL MECHANICS II

Q1. a) i) The Boltzmann distribution at a temperature T can be written in the following form:

$$\frac{n_i}{n_0} = \frac{g_i}{g_0}\exp(-\varepsilon_i/k_BT)$$

where ni and n0 are the populations in state i and the ground state respectively. Explain the meaning of the terms g_i, g_0 and ε_i.

ii) The molecular partition function q is defined as

$$q = \sum_{i=0}^{\infty} g_i \exp(-\varepsilon_i/k_BT)$$

Show that the above equation for n_i/n_0 may be rewritten as

$$\frac{n_i}{N} = \frac{g_i \exp(-\varepsilon_i/k_BT)}{q}$$

where N is the total number of molecules.

iii) The molecular partition functions for translation, rotation and vibration of CO at 298 K in a volume of 1 m^3 are 1.2×10^{32}, 109 and 1.00003 respectively. Comment on the relative magnitudes of these values, given that for CO the rotational constant B = 1.9 cm^{-1}, and the first vibrational level lies 2143 cm^{-1} above the v = 0 ground state. [k^BT/hc = 200 cm-1 at 298 K].

b) The partition function q_{vib} for a harmonic oscillator is given by

$$q_{vib} = [\,1 - \exp(-hc\tilde{\nu}/k_BT)]^{-1}$$

where $\tilde{\nu}$ is the wavenumber of the vibration.

From the expression for the mean vibrational energy per molecule,

$$\frac{E_{vib}}{N_A} = k_BT^2\frac{\partial \ln q_{vib}}{\partial T}$$

derive an expression for E_{vib}/N_A and show that at high temperature ($hc\tilde{\nu} \ll k_BT$) the value tends to the classical limit of k_BT. [Note that $e^x = 1 + x + x^2/2! + \ldots$]

c) A two-level system, with both levels non-degenerate, is at equilibrium at a temperature T. Calculate the relative populations of the levels and the average energy per molecule, and show that the heat capcacity of the system tends to zero at high temperature (when the separation of the levels is much less than k_BT.

Q2. Write down an expression for the molecular partition function (q) as a sum over *energy levels*, identifying clearly the quantities therein. Explain why q may be separated into a product of contributions from the various molecular modes of motion.

The rotational energy levels of a (heteronuclear) diatomic molecule are given by $E_J = BhcJ(J+1)$, with B the rotational constant such that $\theta = Bhc/k_B$ is the characteristic rotational temperature.

a) Explain why the fraction of molecules found in the rotational energy levels specified by the quantum number J is

$$f(J) = \frac{2J+1}{q_{rot}} \exp\left(-\frac{\theta}{T} J(J+1)\right)$$

where q_{rot} is the rotational partition function.

b) Write down the expression for q_{rot} and, by transforming the sum to a suitable integral, obtain q_{rot} in the high-temperature limit $T \gg \theta$.

c) To a first approximation the intensity of a rotational absorption transition from $J \rightarrow J'$ is determined by f(J). Explain briefly why this is so, and show that the line with maximum spectral intensity ($J = J_{max}$) corresponds to

$$J_{max} = \sqrt{\frac{T}{2\theta}} - \frac{1}{2}$$

d) The Stokes branch of the pure rotational Raman spectrum of the (heteronuclear) molecule consists of approximately equally spaced lines separated by 9.8 cm^{-1}. Identify which rotational transition has maximum intensity at a temperature T = 298 K. ($k_BT/hc = 207.2\ cm^{-1}$ at T = 298 K).

Q3. Statistical mechanics gives the following result for the equilibrium constant K ($\equiv K_p$) of a gas phase reaction.

$$K = \prod_j \left(\frac{q_j^{\circ}}{N_A}\right)^{\nu_J} \exp(-\Delta E_0/RT)$$

a) Explain carefully the meaning of the quantities appearing in this expression.

Consider the thermal ionization of an atomic species A,

$$A \rightleftharpoons A^+ + e^-$$

with ionization energy I. For both A and A^+, you need retain only the lowest energy electronic state ^{2S+1}L arising from the appropriate ground electronic configuration; the difference in energy between the spin-orbit components (J) of these states may be neglected.

b) Show that the equation for this equilibrium (the Saha equation) may be expressed as

$$K = \frac{2k_BT}{P^{\ominus}\Lambda^3(T)}\frac{g_{A^+}}{g_A}\exp(-I/RT)$$

where $\Lambda(T)$ is the de Broglie wavelength of the electron, and g_{A^+} and g_A denote respectively the degeneracies of the A^+ and A electronic ground states.
[Note that for a particle of mass *m*, the translational partition function is given by $q_{tr} = V/\Lambda^3(T)$, where $\Lambda(T) = h/(2\pi m k_B T)^{1/2}$.]

c) Calculate K at T = 4000 K for the thermal ionization of carbon atoms. For carbon, I = 1086 kJ mol^{-1}.

d) In assuming Boltzmann statistics, the above result for K effectively treats the electrons as classical particles. This is valid only if $\Lambda(T) \ll (V/N_e)^{1/3}$, where N_e/V is the number density of electrons. For T = 4000 K and $P/P^{\ominus} = 10^{-4}$, the fraction of ionized carbon atoms is 1.7×10^{-4}. Can the quantum mechanical nature of the electrons be neglected under these conditions? Explain your reasoning.