Physics 408 -- Exam 3 **Name**____

You are graded on your work, with partial credit where it is deserved.

Please give clear, well-organized solutions.

1. Recall that the Gibbs free energy is defined by

$$G = \langle E \rangle - TS + PV$$

where $\langle E \rangle$, T, S, P, and V are (as usual) the energy, temperature, entropy, pressure, and volume.

(a) (5) What are the natural variables of G?

(b) (5) Obtain a general expression for dG in terms of dT, dP, and dN.

(c) (5) By using the appropriate second derivatives of G, relate $\left(\frac{\partial V}{\partial T}\right)_P$ to $\left(\frac{\partial S}{\partial P}\right)_T$.

(d) (5) Using the result of part (c), describe the behavior of the thermal expansion coefficient α as $T \to 0$ (and explain your reasoning).

(e) (5) For a specific system you are given that

$$G = -NkT \ln\left(\frac{aT^{7/2}}{P}\right)$$

where N is the number of particles, k is Boltzmann's constant, and a is a constant. Calculate the entropy S, and from S the heat capacity at constant pressure C_P.

(f) (5) Calculate the volume V in terms of N, T, and P.

$h = 6.63 \times 10^{-34}$ J s	[Planck's constant]	$k = 1.38 \times 10^{-23}$ J/K	[Boltzmann's constant]
$m_e = 9.11 \times 10^{-31}$ kg	[mass of electron]	1 eV $= 1.60 \times 10^{-19}$ J	

2. In class we derived the equilibrium law of mass action

$$\prod_i [i]^{b_i} = K(T) \quad , \quad K(T) = \prod_i \left[\lambda_i^{-3} Z_i(\text{int})\right]^{b_i} \quad , \quad \lambda_i = \frac{h}{\left(2\pi m_i kT\right)^{1/2}}$$

where $[i]$ is the number density of species i and the other quantities should look familiar.

(a) (10) Consider the reaction

$$\text{Ca} \rightleftarrows \text{Ca}^+ + e \ .$$

Given that the calcium atom Ca has $Z_i(\text{int}) = e^{-\varepsilon_0/kT}$, that the calcium ion Ca^+ has $Z_i(\text{int}) = 2$, and that their masses are equal to a good approximation, obtain an expression for

$$\frac{\left[\text{Ca}^+\right][e]}{[\text{Ca}]}$$

in terms of λ_e and the energy ε_0 of the neutral atom Ca relative to the ion Ca^+.

(b) (10) Given that $\varepsilon_0 = -6.113$ eV, for a stellar atmosphere with $T = 6000$ K and $[e] = 10^{20}$ electrons per cubic meter, calculate the ratio $\dfrac{\left[\text{Ca}^+\right]}{[\text{Ca}]}$.

3. (a) (5) In the canonical ensemble (i.e., for a system with a well-defined temperature T, volume V, and number of particles N), what is the probability p_j that a system is in a quantum state j with energy E_j?

Give p_j in terms of E_j, T, and the partition function Z, of course.
(This is one of the simplest and most central expressions in our course.)

(b) (5) Solve for E_j in terms of p_j, $\ln Z$, and T.

(c) (5) Substitute your result from part (b) into $\langle E \rangle = \sum_j E_j p_j$ to obtain the thermodynamic energy $\langle E \rangle$ in terms of $\sum_j p_j \ln p_j$, T, and $\ln Z$.

(d) (5) By equating (i) the definition of the Helmholtz free energy F to (ii) the fundamental expression for F in terms of $\ln Z$, show that the entropy is given by $S = \frac{\langle E \rangle}{T} + k \ln Z$.

(e) (5) Finally, obtain the very fundamental expression for the entropy S in terms of $\sum_j p_j \ln p_j$.

4. There is a more general version of the equipartition theorem than the one in the textbook. Start with the classical expression

$$\left\langle \frac{\partial \varepsilon}{\partial x} x \right\rangle = \frac{\int d(others)\, e^{-E'(others)/kT} \int_{-X}^{X} dx \frac{\partial \varepsilon(x)}{\partial x} x\ e^{-\varepsilon(x)/kT}}{\int d(others)\, e^{-E'(others)/kT} \int_{-X}^{X} dx\, e^{-\varepsilon(x)/kT}}$$

where the total energy E has been separated into the part $\varepsilon(x)$ which depends on some variable x (a coordinate or a momentum) and a remainder E' which does not depend on x, and where $\varepsilon(x) \to \infty$ as $x \to \pm X$. (For a momentum, the limits of integration are $\pm\infty$, and for a coordinate they are the limits in space imposed by walls or other boundaries.)

(a) (15) Using integration by parts, and carefully showing all your steps, obtain the general result

$$\left\langle \frac{\partial \varepsilon}{\partial x} x \right\rangle = \text{constant} \times T$$

while also obtaining the constant.

(b) (10) For a polyatomic molecule, with 3 rotational degrees of freedom plus the usual 3 translational degrees of freedom, the total kinetic energy is

$$\varepsilon_{total} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} + \frac{J_1^2}{2I_1} + \frac{J_2^2}{2I_2} + \frac{J_3^2}{2I_3}$$

where the J_i are angular momenta in a rotating frame of reference whose axes coincide with the principal axes of rotation, for which the moments of inertia are the I_i.

Use the result of part (a) to obtain the heat capacity at constant volume C_V for an ideal gas of such polyatomic molecules. Assume that $kT \ll h\nu_i$ for all the vibrational frequencies ν_i.

Have a good Wednesday!