**Chemistry 1480, Hour Exam 1,** Feb. 7, 2007.

This exam consists of four (4) problems. Please work them all, and provide brief descriptions of your reasoning as appropriate. GOOD LUCK! [Note the designation $\beta \equiv (k_B T)^{-1}$, where $k_B$ is Boltzmann's constant and $T$ is the absolute temperature in degrees K.]

**1)** [25 %] A spin-1 particle interacting with a constant magnetic field *B* can be described as a <u>three</u> state system with energy levels $E = -\mu B, 0, \mu B$ (the constant $\mu$ is essentially the permanent magnetic moment of the particle). If the system is placed in thermal contact with a heat bath at temperature *T*,

a) Show that the partition function for the system is:

$$q = 1 + 2\cosh(\beta \mu B)$$

b) Obtain an expression for the average energy $\bar{E}$ of the system. What is the value of $\bar{E}$ when $T = \infty$ ?

c) Figure 1 shows three possibilities (A,B,C) for the graph of the system's constant volume heat capacity $C_V$ vs. absolute temperature T. Which curve is qualitatively correct? What is the "fatal flaw" in each of the other two curves?

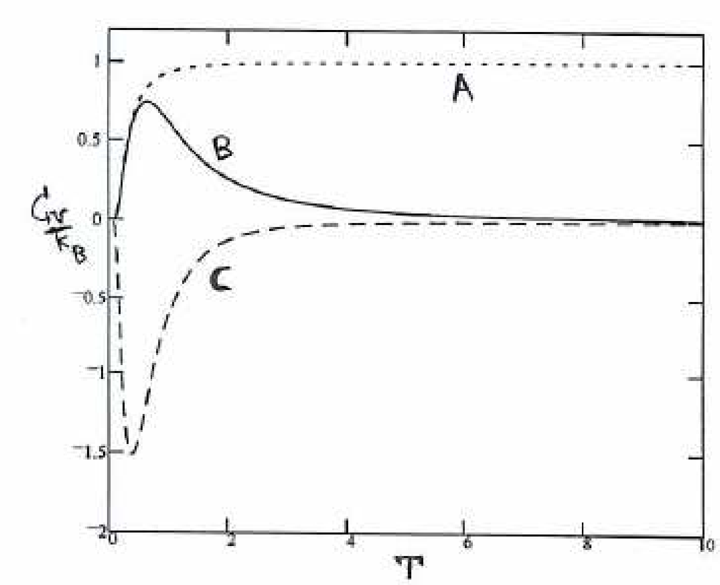


Figure 1.

**2)** [25 %] Consider a monatomic ideal gas, whose entropy is described by the Sackur-Tetrode Equation.

a) Show that at a given pressure and temperature, the difference in molar entropies between a gas of atoms of type A and a gas of atoms of type B has the form:

$$S_m^{(B)} - S_m^{(A)} = \kappa R \ln(m_B / m_A)$$

where $S_m^{(A)}$ is the molar entropy of species A, and analogously for species B; furthermore, *R* is the ideal gas constant, and $\kappa$ is a dimensionless numerical coefficient which *you are to compute*. [Note: Assume here that the ground electronic states of atoms A and B are nondegenerate.]

b) Given that the standard (i.e., $p = 1$ atm) molar entropy of gaseous argon [atomic mass = 40 amu] at $100^{\circ}$C is 19.4 $R$, use the result of part a) to deduce the standard entropy of gaseous xenon [atomic mass = 131 amu] at the same temperature. Please state your answer in units of *R*.

**3)** [25 %] Consider a particle characterized by an infinite number of nondegenerate states corresponding to energy levels $E_n = n\varepsilon$, $n = 0,1,2,\ldots$, with $\varepsilon > 0$ being an energy parameter (i.e., the "quantum of energy"). If this particle is placed in contact with a heat bath at absolute temperature *T*:

a) Show that the partition function for this system is:

$$q = [1 - e^{-\beta\varepsilon}]^{-1}$$

[Hint: $1 + x + x^2 + \ldots = (1-x)^{-1}$ for $|x| < 1$.]

b) Show that the average energy of the system is:

$$\bar{E} = \varepsilon / (e^{\beta\varepsilon} - 1)$$

In particular, determine $\bar{E}$ at $T = 0$, and briefly explain your result.

c) Give a general formula for the entropy $S$ of this particle at temperature *T*. [Hint: simply combine the results of parts a) and b) in an appropriate fashion.]

In particular, show that as $T \to \infty$, $S \to k_B \ln(k_B T / \varepsilon)$.

**4)** [25%] In class we noted an "improved" version of Stirling's Approximation, namely:

$$\ln N! \cong N \ln N - N + \tfrac{1}{2}\ln(2\pi N) \qquad [1]$$

a) Consider the binomial coefficient $c(n) \equiv N!/n!(N-n)!$ for a fixed value of N. Use the improved Stirling's approximation above to show that:

$$c(N/2) = \frac{N!}{[(\frac{N}{2})!]^2} \cong 2^N \sqrt{\frac{2}{\pi N}} \qquad [2]$$

b) In class, we used the simple Stirling's approximation (the right hand side of Eq. [1] without the last term) to show that for large N, $c(n)/c(N/2) \cong \exp[-\frac{2}{N}(n - N/2)^2]$. Coupling this with Eq. [2] implies the following approximation to $c(n)$, denoted as $c_{ap}(n)$:

$$c_{ap}(n) \cong 2^N \sqrt{\frac{2}{\pi N}} \exp[-\frac{2}{N}(n - N/2)^2]$$

Calculate an approximation to the sum $S_{ap} = \sum_{n=0}^{N} c_{ap}(n)$. [Hint: the integral $\int_{-\infty}^{\infty} dx \exp(-Ax^2) = \sqrt{\pi / A}$ may be of use.] Compare the result you obtain in this way with the exact summation formula $\sum_{n=0}^{N} c(n) = 2^N$ .