CYL501 Final Exam

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1. A cylinder contains a perfect gas in thermodynamic equilibrium at p, V, T, U, and S. The cylinder is surrounded by a heat reservoir at the same temperature T. The cylinder walls and piston can be either perfect thermal conductors or perfect thermal insulators. The piston is moved to produce a small volume change $\pm\Delta V$. For each of the five processes below show whether the changes in the other quantities are positive, negative, or zero. (a) $(+\Delta V)$ (slow) (conduct) (b) $(+\Delta V)$ (slow) (insulate) (c) $(+\Delta V)$ (fast) (insulate) (d) $(+\Delta V)$ (fast) (conduct) (e) $(-\Delta V)$ (fast) (conduct).

2. For each of the following thermodynamic conditions, describe a system, or class of systems (the components or range of components, temperatures, etc..), which satisfies the condition. Confine your attention to classical, single component, chemical systems of constant mass. (a) $\left(\frac{\partial U}{\partial V}\right)_T = 0$ (b) $\left(\frac{\partial S}{\partial V}\right)_P < 0$ (c) $\left(\frac{\partial T}{\partial S}\right)_P = 0$ (d) $\left(\frac{\partial S}{\partial V}\right)_T = 0$ (e) $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial V}\right)_S$.

3. (a) Write a formula for the number of ways (Ω) in which H heads and T tails can occur in a series of N tosses of a well-balanced coin.
   (b) For a series of N coin tosses, how many heads and tails are there in the predominant configuration?
   (c) A ratio, $A_{H,T} = \frac{\Omega_{HT}}{\Omega_{\text{mp}}}$, where Ω_{HT} and Ω_{mp} are the number of microstates with H heads and T tails and the number of microstates in the predominant configuration respectively, is defined. Use Stirling's approximation to obtain an expression for $\log A_{HT}$.
   (d) For a series of 10 coin tosses, determine the number of microstates in the predominant configuration. Obtain $A_{4,6}$ exactly and using Stirling's approximation.
   (e) For a series of 1000 coin tosses, use Stirling's approximation to determine $A_{400,600}$.
   (f) Explain the difference in the A-ratios for the 4-6 and 400-600 configurations computed above.

4. Consider an assembly of units in which there are ω_1 states in the first excited electronic level of energy ϵ_1 that is not too much greater than the energy ϵ_0 of the ground electronic level, which has ω_0 states.

   (a) Taking as your zero of energy $\epsilon_0 \equiv 0$, and using ω for the ratio ω_1/ω_0, show that
   $$Z = \omega_0 \left(1 + \omega \exp\left(-\frac{\epsilon_1}{kT}\right)\right).$$

(b) For an N-unit assembly, show that

$$< E >= \frac{\omega N \epsilon_1}{\left(\exp\left(+\frac{\epsilon_1}{kT}\right) + \omega\right)}.$$

Show that $< E > \to 0$ as $T \to 0$. What is $< E >$ at high temperature?

(c) Show that

$$C_V = \omega R \left(\frac{\epsilon_1}{kT}\right)^2 \frac{\exp\left(\frac{\epsilon_1}{kT}\right)}{\left(\exp\left(\frac{\epsilon_1}{kT}\right) + \omega\right)^2}.$$

Determine the limiting values of C_V at low and high temperatures.

(d) Between the two limiting values C_V reaches a maximum value. Show that the maximum value is reached when

$$\frac{\epsilon_1}{kT} = 2.303 \left[\log \omega + \log \left(\frac{\left(\frac{\epsilon_1}{kT}\right) + 2}{\left(\frac{\epsilon_1}{kT}\right) - 2}\right)\right]$$

(e) Nitric oxide, NO, has $\omega_0 = \omega_1 = 2$, and $\epsilon_1 = 2.4 \times 10^{-14}$ erg. For this substance, at what temperature will C_V reach its maximum value, what is that value, and what is likely to be the total heat capacity of NO at the temperature in question?

5. (a) Give Boltzmann's statistical definition of entropy and present its physical meaning briefly but clearly.

(b) A two-level system of $N = n_1 + n_2$ particles is distributed among two states 1 and 2 with energies E_1 and E_2 respectively. The system is in contact with a reservoir at temperature T. If a single quantum emission into the reservoir occurs, population changes from $n_2 \to n_2 - 1$ and $n_1 \to n_1 + 1$ take place in the system. For $n_1 >> 1$ and $n_2 >> 1$, obtain the expression for the entropy change of

i. the two-level system, and of
ii. the reservoir, and finally
iii. from i. and ii. derive the Boltzmann relation for n_1 and n_2.