1. Consider a three-level single particle system with six microstates with energies 0, ε, ε, ε, 2ε, 2ε. What is the mean energy of the system if it is in equilibrium with a bath at temperature T? In the region where $\beta\varepsilon \to 0$, what will the graph of heat capacity of the sytem as a function of ε look like at a constant temperature?

Ans. $U = \frac{\sum_j E_j e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} = \frac{3\varepsilon.e^{-\beta\varepsilon}+2\varepsilon.2e^{-2\beta\varepsilon}}{1+3e^{-\beta\varepsilon}+2e^{-2\beta\varepsilon}} = \varepsilon.\frac{3e^{-\beta\varepsilon}+4e^{-2\beta\varepsilon}}{1+3e^{-\beta\varepsilon}+2e^{-2\beta\varepsilon}}$

heat capacity, $C_V = \frac{\partial U}{\partial T} = -\frac{\beta}{T}\frac{\partial U}{\partial \beta} = -\frac{\beta\varepsilon}{T}.\left[-\varepsilon.\frac{3e^{-\beta\varepsilon}+8e^{-2\beta\varepsilon}}{1+3e^{-\beta\varepsilon}+2e^{-2\beta\varepsilon}} + \varepsilon.\frac{\left(3e+4e^{-2\beta\varepsilon}\right)\left(3e^{-\beta\varepsilon}+4e^{-2\beta\varepsilon}\right)}{(1+3e^{-\beta\varepsilon}+2e^{-2\beta\varepsilon})^2}\right] = \text{const}.\varepsilon^2$

$\therefore$ the graph will look like a parabola.

2. The atomic energy states of F are given as follows: $E_{^2P_{\frac{3}{2}}} = 0$; $E_{^2P_{\frac{1}{2}}} = 404.0\text{cm}^{-1}$. Show that less than three percent of F atoms occupy the first excited state at 200K. $[hc/k_B = 1.44$ cm-deg (K)$]$ and degeneracy of the state ^2P_j is $2j+1$.

Ans. fraction of F atoms in the excited state $= \frac{2\times\frac{1}{2}+1}{2\times\frac{3}{2}+1}.e^{-\frac{1.44\times 404}{200}} = \frac{1}{2}e^{-2.9} = \frac{0.055}{2} = 2.75\%$

3. Obtain the value for: $\frac{\Theta_{x,H_2}}{\Theta_{x,D_2}}$, for x=v(vibrational) at high temperatures, without using the Tables

Ans. The equilibrium bond distance and the force constant is determined by electronic effects, so it will be the same for both H_2 and D_2. But the reduced masses will change. The symmetry number for both is 2.

$$\frac{\Theta_{x,H_2}}{\Theta_{x,D_2}} = \frac{\nu_{D_2}}{\nu_{H_2}} = \sqrt{\frac{\mu_{H_2}}{\mu_{D_2}}} = \sqrt{\frac{m_H}{m_D}} = \frac{1}{\sqrt{2}}$$

4. Explain qualitatively why the pressure of an ideal Fermi gas is different from that of the classical ideal gas. Mention also if it is lower or higher.

Ans. For the classical ideal gas, the molecules occupy continuous energy states and there is no restriction on how many molecules may be in a certain energy state. For the Fermi gas, there is a restriction that only one molecule may be in a certain energy state. This results in a 'quantum' repulsive interaction that increases the pressure of the gas.

5. Given that for a N-particle system of volume V, the number of energy states for an energy U is given by $\Omega(U, N, V) = \frac{V^N}{h^{3N}N!}.\frac{(2\pi mU)^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!}$,obtain an expression for the entropy as a function of U and N, and obtain an expression for the temperature of the system (use microcanonical ensemble theory and Stirling's approximation).

Ans. $S(U, N, V) = k_B \ln\Omega = Nk_B\left\{\ln\frac{V}{N} + \frac{1}{2}\ln\left(\frac{2U}{3N}\right) + \ln\frac{(2\pi m)^{\frac{3}{2}}e^{\frac{5}{2}}}{h^3}\right\}$

$= k_B \ln\left[\frac{V^N}{h^{3N}N!}.\frac{(2\pi mU)^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!}\right]$

Use Stirling's approximation, $\ln N! = N\ln N - N$, or, $N! = \left(\frac{N}{e}\right)^N$

$S = k_B \ln\left[\left(\frac{eV}{h^3N}\right)^N.\left(\frac{2e.2\pi emU}{3N}\right)^{\frac{3N}{2}}\right] = Nk_B\left\{\ln\frac{V}{N} + \frac{3}{2}\ln\left(\frac{2U}{3N}\right) + \ln\frac{(2\pi m)^{\frac{3}{2}}e^{\frac{5}{2}}}{h^3}\right\}$

$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{3}{2}\frac{Nk_B}{U}$