1. Consider a three-level single particle system with six microstates with energies 0, 0, ε, 2ε, 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 system as a function of ε look like at a constant temperature?

Ans. $U = \frac{\sum\limits_j E_j e^{-\beta E_j}}{\sum\limits_j e^{-\beta E_j}} = \frac{\varepsilon.e^{-\beta\varepsilon}+2\varepsilon.3e^{-2\beta\varepsilon}}{2+e^{-\beta\varepsilon}+3e^{-2\beta\varepsilon}} = \varepsilon.\frac{e^{-\beta\varepsilon}+6e^{-2\beta\varepsilon}}{2+e^{-\beta\varepsilon}+3e^{-2\beta\varepsilon}}$

heat capacity, $C_V = \frac{\partial U}{\partial T} = -\frac{\beta}{T}\frac{\partial U}{\partial \beta} = -\frac{\beta\varepsilon}{T}.\left[-\varepsilon.\frac{e^{-\beta\varepsilon}+12e^{-2\beta\varepsilon}}{2+e^{-\beta\varepsilon}+3e^{-2\beta\varepsilon}} + \varepsilon.\frac{\left(e^{-\beta\varepsilon}+6e^{-2\beta\varepsilon}\right)\left(e^{-\beta\varepsilon}+6e^{-2\beta\varepsilon}\right)}{\left(2+e^{-\beta\varepsilon}+3e^{-2\beta\varepsilon}\right)^2}\right] = \text{const}.\varepsilon^2$

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

2. Obtain (briefly derive) the criterion for an ideal gas like system to obey Classical statistics. Give one example of a real system where this criterion is violated.

Ans. Boltzmann statistics is valid if number of energy states available is large enough, $\Phi(\varepsilon) \gg N$

A quantum mechanical system approaches classical behaviour if the difference in energy between states is very small and they can be treated as nearly continuous

We require for Maxwell-Boltzmann statistics to be valid,

accessible states $\gg$ #particles

using the particle in a box model for an ideal system ,

$\frac{\pi}{6}\left(\frac{8m\varepsilon}{h^2}\right)^{\frac{3}{2}} V \overset{\varepsilon=\frac{3}{2}k_BT}{=} \frac{\pi}{6}\left(\frac{12mk_BT}{h^2}\right)^{\frac{3}{2}} V \gg N$

or, $\frac{\pi}{6}\left(\frac{12mk_BT}{h^2}\right)^{\frac{3}{2}} \gg \frac{N}{V}$: this is the required criterion

We can also put it like $\frac{6N}{\pi V}\left(\frac{h^2}{12mk_BT}\right)^{\frac{3}{2}} \ll 1$

examples where this criterion is violated : liquid He and electrons in metals, for which $\frac{6N}{\pi V}\left(\frac{h^2}{12mk_BT}\right)^{\frac{3}{2}}$ is 1.6 and 1465 respectively

3. Using the canonical ensemble theory results, show that the information entropy $S = -k_B \sum\limits_j P_j \ln P_j$, where P_j =the probability that the system is in the energy state E_j, is the same as the statistical expression for the probability.

Ans. $P_j = \frac{e^{-\beta E_j}}{Q}$

$\therefore S = -k_B \sum\limits_j P_j \ln P_j = -k_B \sum\limits_j \frac{e^{-\beta E_j}}{Q} \ln\left(\frac{e^{-\beta E_j}}{Q}\right) = -\frac{k_B}{Q}\sum\limits_j e^{-\beta E_j} \ln\left(e^{-\beta E_j}\right) + \frac{k_B}{Q}\sum\limits_j e^{-\beta E_j} \ln Q$

$= \frac{\beta k_B}{Q}\sum\limits_j E_j e^{-\beta E_j} + \frac{k_B}{Q}.Q\ln Q = \frac{U}{T} + k_B \ln Q$

4. Show that Boltzmann statistics is a limiting case of quantum statistics.

Ans. Quantum statistics gives : $\ln \Xi = \frac{pV}{k_BT} = \pm\sum\limits_k \ln\left(1 \pm \lambda e^{-\beta\varepsilon_k}\right)$

For small λ, we can expand the logarithm and use only the first term $[\ln(1+x) \approx x]$:

$\beta pV = \lambda \sum\limits_k e^{-\beta\varepsilon_k} = \lambda q$

$\therefore \Xi = e^{\lambda q} = \sum\limits_{N=0}^{\infty} \frac{(\lambda q)^N}{N!}$

But $\Xi(V,T,\mu) = \sum\limits_N Q(N,V,T)e^{\beta\mu N} = \sum\limits_N Q(N,V,T)\lambda^N$

$\therefore Q(N,V,T) = \frac{q^N}{N!}$ which is Boltzmann statistics.

5. Obtain the value for: $\frac{\Theta_{x,H_2}}{\Theta_{x,D_2}}$, for x=r(rotational) 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.

$\frac{\Theta_{x,H_2}}{\Theta_{x,D_2}} = \frac{I_{D_2}}{I_{H_2}} = \frac{\mu_{D_2}}{\mu_{H_2}} = \frac{m_D}{m_H} = 2$