Take_home-Statistical_Thermodynamics-Answers-30Sept13

1. N independent particles exist in one of the 3 non-degenerate energy levels of energies −E, 0, +E. The system is in contact with a thermal reservoir at temperature T. What is the partition function of the system? Use canonical ensemble to show that
   (i) The maximum possible entropy in the limit T→1 is S = Nk ln 3
   (ii) The minimum possible energy in the limit T→0 is E = −NE

(i) $$S = \frac{\bar{E}}{T} + Nk \ln q$$

$$S = \frac{\bar{E}}{T} + Nk \ln (1 + e^{E/kT} + e^{-E/kT})$$

$$T \to \infty$$

$$S = 0 + Nk \ln 3$$

$$\Rightarrow \boxed{S = Nk \ln 3}$$

(ii) $$\bar{E} = NkT^2 \frac{\partial \ln q}{\partial T}$$

$$q = 1 + e^{E/kT} + e^{-E/kT}$$

$$\ln q = \ln (1 + e^{E/kT} + e^{-E/kT})$$

$$\frac{\partial \ln q}{\partial T} = \frac{1}{1 + e^{E/kT} + e^{-E/kT}} \left(-\frac{E}{kT^2} e^{E/kT} + \frac{E}{kT^2} e^{-E/kT}\right)$$

$$\frac{\partial \ln q}{\partial T} = -\frac{E}{kT^2} \frac{(e^{E/kT} - e^{-E/kT})}{1 + e^{E/kT} + e^{-E/kT}}$$

$$\bar{E} = -NE \frac{(e^{E/kT} - e^{-E/kT})}{1 + e^{E/kT} + e^{-E/kT}}$$

$$T \to 0 \qquad \bar{E} = -NE \frac{e^{E/kT}}{e^{E/kT}} = -NE$$

$$\Rightarrow \boxed{\bar{E} = -NE}$$

$$T \to \infty \qquad \bar{E} = -NE \times 0 = 0$$

2.Consider a system of distinguishable particles having only two non-degenerate energy levels separated by an energy which is equal to the value of kT at 10K. Calculate at 10K (a) the ratio of populations in the two states (b) the molecular partition function (c) the molar energy (d) the molar heat capacity (e) the molar entropy.

Energy separation is $\varepsilon = k \times (10\,k)$

(a) $\frac{n_1}{n_0} = e^{-\beta(\varepsilon_1 - \varepsilon_0)} = e^{-\beta\varepsilon} = e^{-10/T}$

$T = 10\,k \qquad \frac{n_1}{n_0} = e^{-1.0} = 0.4$

(b) $q = \sum_i g_i e^{-\varepsilon_i/kT} = e^0 + e^{-1.0} = 1.4$

(c) $\bar{E} = NkT^2 \frac{\partial \ln q}{\partial T} \qquad \frac{\bar{E}}{n} = N_A kT^2 \frac{\partial \ln q}{\partial T}$

Molar energy: $\bar{E}_m = RT^2 \frac{\partial \ln q}{\partial T}$

$q = 1 + e^{-10/T}$

$\ln q = \ln(1 + e^{-10/T})$

$\frac{\partial \ln q}{\partial T} = \frac{1}{1+e^{-10/T}} \left(\frac{10}{T^2} e^{-10/T}\right)$

$\bar{E}_m = \frac{R\,10}{1+e^{-10/T}} e^{-10/T} = \frac{10\,R}{e^{10/T}+1} \qquad$ At $T = 10\,K$

$= \frac{10(K) \times 8.314\,(J\,K^{-1}\,mol^{-1})}{3.718} = 22\,J\,mol^{-1}$

(d) $C_{v,m} = \left(\frac{\partial \bar{E}_m}{\partial T}\right)_v = \frac{\partial}{\partial T}\left[\frac{10R}{(e^{10/T}+1)}\right] = 10R\,(e^{10/T}+1)^{-1}$

$= -10R\,(e^{10/T}+1)^{-2}\,10\left(-\frac{1}{T^2}\right) e^{10/T}$

$= \frac{100\,R}{T^2} \frac{e^{10/T}}{(e^{10/T}+1)^2} = R\frac{e}{(1+e)^2}$

$= 1.6\,J\,K^{-1}\,mol^{-1}$

(e) $$S_m = \frac{\bar{E}_m}{T} + R\ln q$$

$$= \frac{22\ \mathrm{J\,mol^{-1}}}{10\ \mathrm{K}} + R\ln 1.4$$

$$= 4.8\ \mathrm{J\,K^{-1}mol^{-1}}$$

3.Calculate the translational partition function of an H_2 molecule confined to a 100 cm^3 vessel at 25°C.

$$q_{trans} = \frac{V}{\Lambda^3} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$$

$1u = 1.66\times10^{-27}$ kg

$m = 2.016\ u$

atomic mass unit

$$\Lambda = \frac{6.626\times10^{-34}\ \mathrm{Js}}{(2\pi \times 2.016\times1.66\times10^{-27}\ \mathrm{kg} \times 4.116\times10^{-21}\ \mathrm{J})^{1/2}}$$

$$= 7.12\times10^{-11}\ \mathrm{m}$$

$$q_{trans} = \frac{1\times10^{-4}\ \mathrm{m^3}}{(7.12\times10^{-11}\ \mathrm{m})^3} = 2.77\times10^{26}$$

4.An electron spin can adopt either of two orientations in a magnetic field, and its energies are $\pm\mu_B\,\beta$, where μ_B is the Bohr magneton (a) Deduce an expression for the partition function and mean energy of the electron. (b) Calculate the relative populations of the spin states at 4K and $\beta = 1.0$T.

$$q = e^{-\mu_B B/kT} + e^{\mu_B B/kT}$$

$$\langle \varepsilon \rangle = \frac{\bar{E}}{N} = kT^2 \frac{\partial \ln q}{\partial T}$$

$$\ln q = \ln\left(e^{-\mu_B B/kT} + e^{\mu_B B/kT}\right)$$

$$\frac{\partial \ln q}{\partial T} = \frac{1}{\left(e^{-\mu_B B/kT} + e^{\mu_B B/kT}\right)} \left(-\frac{\mu_B B}{k}\left(-\frac{1}{T^2}\right) e^{-\mu_B B/kT} + \frac{\mu_B B}{k}\left(-\frac{1}{T^2}\right) e^{\mu_B B/kT}\right)$$

$$\frac{\partial \ln q}{\partial T} = \frac{\mu_B B}{kT^2} \frac{e^{-\mu_B B/kT} - e^{\mu_B B/kT}}{e^{-\mu_B B/kT} + e^{\mu_B B/kT}}$$

$$\langle \varepsilon \rangle = \mu_B B \frac{e^{-\mu_B B/kT} - e^{\mu_B B/kT}}{e^{-\mu_B B/kT} + e^{\mu_B B/kT}}$$

The relative populations

$$\frac{n_1}{n_2} = e^{-\beta \Delta \varepsilon} = e^{2\mu_B B/kT}$$

$$\frac{2\mu_B B}{kT} = \frac{2 \times 9.274 \times 10^{-24}\ \mathrm{J\,T^{-1}} \times 1.0\ \mathrm{T}}{1.381 \times 10^{-23}\ \mathrm{J\,K^{-1}}\ (4\ \mathrm{K})} = 0.71$$

5.Calculate the fraction of $N_2(g)$ molecules in the v = 0 and v = 1 vibrational states at 300K, given that $h\nu/k_B$ = 3374K.

$$q_{vib} = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta hc\bar{\nu}\left(v+\frac{1}{2}\right)} = e^{-\beta hc\bar{\nu}/2} \sum_{n=0}^{\infty} e^{-\beta hc\bar{\nu}v} = \frac{e^{-\beta hc\bar{\nu}/2}}{1-e^{-\beta hc\bar{\nu}}}$$

$$\text{Fraction of molcules in vth state, } f_v = \frac{e^{-\beta hc\bar{\nu}\left(v+\frac{1}{2}\right)}}{q_{vib}} = \frac{e^{-\beta hc\bar{\nu}\left(v+\frac{1}{2}\right)}}{\dfrac{e^{-\beta hc\bar{\nu}/2}}{1-e^{-\beta hc\bar{\nu}}}} = \left(1-e^{-\beta hc\bar{\nu}}\right)e^{-\beta hc\bar{\nu}v}$$

$$f_v = \left(1-e^{-\frac{hc\bar{\nu}}{kT}}\right)e^{-\frac{hc\bar{\nu}}{kT}v} = \left(1-e^{-\frac{h\nu}{kT}}\right)e^{-\frac{h\nu}{kT}v}$$

$$\frac{h\nu}{kT} = \frac{3374K}{300K} = 11.25$$

$$f_{v=0} = \left(1-e^{-11.25}\right)e^{-0} = 0.999$$

$$f_{v=1} = \left(1-e^{-11.25}\right)e^{-11.25} = 1.305\times10^{-5}$$

6.The molecules of a gas have two states of internal energy with statistical weights g_1, g_2 and energies 0, ε respectively. Calculate the contribution of these states to the specific heat of the gas.

$$q = g_1 + g_2\, e^{-\varepsilon/kT}$$

$$P_1 = \frac{n_1}{N} = \frac{g_1\, e^{-0/kT}}{q} = \frac{g_1}{q}$$

$$P_2 = \frac{n_2}{N} = \frac{g_2\, e^{-\varepsilon/kT}}{q}$$

$$\bar{\varepsilon} = \sum_{i=1}^{2} \varepsilon_i P_i$$

$$= \frac{\epsilon g_2\, e^{-\epsilon/kT}}{g_1 + g_2\, e^{-\epsilon/kT}}$$

$$\bar{E} = N\bar{\epsilon} = \frac{N\epsilon g_2\, e^{-\epsilon/kT}}{g_1 + g_2\, e^{-\epsilon/kT}}$$

$$C_v = \left(\frac{\partial E}{\partial T}\right)_V = \frac{N\epsilon^2 g_1 g_2\, e^{\epsilon/kT}}{kT^2\left(g_1\, e^{\epsilon/kT} + g_2\right)^2}$$

7.A gas is composed of three atoms of Xe with atomic partition function, q_{Xe} and four atoms of Ar with atomic partition function, q_{Ar}. Write down the total partition function for this system.

Solution :

Xe and Ar atoms are distinguishable from each other and they should be considered separately.

$$Q = \left(\frac{q_{Xe}{}^{3}}{3!}\right)\left(\frac{q_{Ar}{}^{4}}{4!}\right) = \frac{q_{Xe}{}^{3} q_{Ar}{}^{4}}{144}$$

8.The entropy of a monoatomic ideal gas is given by the following equation

$$S = Nk_B\left[\ln\left\{\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{\frac{3}{2}}\right\} + \frac{5}{2}\right]$$ Using the fundamental equation

dU = TdS – PdV, obtain the ideal gas law from the above equation.

Solution :

From, $dU = TdS - PdV$, we obtain, $\frac{\partial U}{\partial V} = T\left(\frac{\partial S}{\partial V}\right)_U - P \Rightarrow \left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T}$

$$S = Nk_B\left[\ln\left\{\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right\} + \frac{5}{2}\right]$$

$$\left(\frac{\partial S}{\partial V}\right)_U = \frac{\partial\left\{Nk_B\left[\ln V + \ln\left\{\frac{1}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right\} + \frac{5}{2}\right]\right\}}{\partial V} = \frac{Nk_B}{V}$$

$$\therefore \frac{P}{T} = \frac{Nk_B}{V} \Rightarrow PV = Nk_B T$$