Q1

(ii)

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

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

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

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

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

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

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

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

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

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

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

$T \to \infty$

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

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

Q2 Energy separation is $\varepsilon = k \times (10 K)$

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

$T = 10 K$ $\quad \frac{n_1}{n_0} = e^{-1.0} = 0.4$

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

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

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

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

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

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

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

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

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

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

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

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

(e) $S_m = \frac{E_m}{T} + R \ln q$

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

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

$1u = 1.66 \times 10^{-27}$ kg

$m = 2.016$ u (atomic mass unit)

Q3 $q_{trans} = \frac{V}{\Lambda^3} = \left(\frac{2\pi m kT}{h^2}\right)^{3/2} V$

$\Lambda = \frac{6.626 \times 10^{-34} \text{ Js}}{(2\pi \times 2.016 \times 1.66 \times 10^{-27} \text{ kg} \times 4.116 \times 10^{-21} \text{J})^{1/2}}$

$= 7.12 \times 10^{-11}$ m

$q_{trans} = \frac{1 \times 10^{-7} \text{m}^3}{(7.12 \times 10^{-11} \text{m})^3} = 2.77 \times 10^{26}$

Q4 $q = \sum_i g_i e^{-\beta \varepsilon_i} = 3 + e^{-\beta \varepsilon_1} + 3 e^{-\beta \varepsilon_2}$

$\beta \varepsilon = \frac{hc\tilde{\nu}}{kT} = \frac{1.4388\, \tilde{\nu} (\text{cm}^{-1})}{T (\text{K})}$

$q = 3 + e^{-(1.4388 \times 3500 / 1900)} + 3 e^{-1.4388 \times 4700 / 1900}$

$= 3 + 0.0706 + 0.085$

$= 3.156$

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

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

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

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

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

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

The relative populations

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

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

6. Write down the molecular partition function with and without degeneracy factor. How is molecular partition function related to canonical partition function for distinguishable and indistinguishable particles?

$$Solution: \quad q = \sum_{levels,\ i} e^{-\beta\varepsilon_i} \quad ; \qquad q = \sum_{levels,\ i} g_i e^{-\beta\varepsilon_i}$$

$$Q_{total} = q_{total}^{N} \quad (distinguishable)$$

$$Q_{total} = \frac{q_{total}^{N}}{N!} \quad (indistinguishable)$$

7. Calculate the ratio of translational partition functions of H_2 and D_2 molecules at 300 K confined separately to a volume of 2.0 cm^3. Ans: 2.83

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

$$\frac{q_{trans}^{D_2}}{q_{trans}^{H_2}} = \left(\frac{m_{D_2}}{m_{H_2}}\right)^{3/2} = 2.828$$

8. Estimate the rotational partition function for HCl at 25°C for J values up to 10. B for HCl is 10.59 cm^{-1}.

$$solution: \quad q_{rot} = \sum_J (2J+1)e^{-\beta hcBJ(J+1)}$$

$$\frac{kT}{hc} = \frac{1.380\times10^{-23}\,JK^{-1}\times298K}{6.626\times10^{-34}\,Js\times3\times10^{8}\,ms^{-1}\times100cm\ m^{-1}} = 206.9cm^{-1}$$

$$q_{rot}^{J=0\ to\ 10} = 1+2.708+3.677+3.787+.....+0.1896+0.0753 \,\square\, 19.9$$

9. Calculate the fraction of N_2(g) molecules in the v = 0 and v = 1 vibrational states at 300K, given that $\frac{h\nu}{k_B} = 3374K$. Ans: Fraction (v=0) ~ 1 and Fraction (v=1) ~ 1.3×10^{-5}

solution:

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

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

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

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

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

$$f_{\text{v}=1} = \left(1-e^{-11.25}\right)e^{-11.25} = 1.305\times 10^{-5}$$

10.What is the electronic partition function for a system with two energy levels which are triply degenerate with energies $E_1 = 0$ and $E_2 = \varepsilon$. What is its value at T = 0 K.

solution:

$$q_{ele} = \sum_j g_j e^{-\beta\varepsilon_j} = 3 + 3e^{-\beta\varepsilon}$$

$$q_{ele}(T = 0K) = 3 + 0 = 3$$