Chem 534: First Exam (100 points total)

Tues, October 13, 2015

Please budget your time carefully and <u>show all work</u>. Miscellaneous equations and other info is on the back page. Write on the back sides of the exam if needed.

(1) (20 pts)

(a) What is required for a *N*-particle canonical partition function Q to be related to the molecular partition function q by $Q = \dfrac{q^N}{N!}$? Be <u>specific</u> about the requirements for <u>both</u> the numerator and denominator.

the particles are independent $_\wedge$ $(E = \epsilon_1 + \epsilon_2 + \cdots \epsilon_N) \Rightarrow q^N$.   *and identical*

the particles are indistinguishable, which leads to division by $N!$ this latter factor is valid under quantum mechanically dilute conditions, i.e., # of states $\gg N$

(b) Starting from fundamental thermodynamic connections, derive an expression for the chemical potential of this system in the Boltzmann limit (i.e., where Boltzmann statistics apply). Show all work. What can you infer about the sign and magnitude of μ?

$$Q = \frac{q^N}{N!} \qquad\qquad A = -kT \ln Q$$

$$\text{since } A = U - TS, \qquad dA = -SdT - pdV + \mu dN$$

$$\text{so } \mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} = -kT\left(\frac{\partial \ln Q}{\partial N}\right)_{T,V}$$

$$\ln Q = N\ln q - \ln N! = N\ln q - N\ln N + N \qquad \text{(Stirling's approx)}$$

$$\mu = -kT\left[\ln q - \ln N - \frac{N}{N} + 1\right] = -kT \ln\left(\frac{q}{N}\right)$$

since $q \gg N$ in Boltzmann limit, μ is negative! large & ~~positive~~

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(2) (10 pts)

Consider a canonical ensemble with partition function Q. Starting from the definition of Q, show that the total internal energy is equal to $kT^2 \left(\dfrac{\partial \ln Q}{\partial T} \right)_{V,N}$.

$$Q = \sum_i e^{-E_i/kT}$$

$$\left(\frac{\partial \ln Q}{\partial T} \right)_{V,N} = \frac{1}{Q} \left(\frac{\partial Q}{\partial T} \right)_{V,N}$$

$$= \frac{1}{Q} \left[\sum_i \frac{1}{kT^2} E_i e^{-E_i/kT} \right]$$

$$= \frac{1}{kT^2} \frac{\sum_i E_i e^{-E_i/kT}}{Q}$$

$$\therefore \; \overline{E}_i = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{V,N}$$

$$= \frac{\overline{E}_i}{kT^2}$$

(3) (10 pts)

A particular system has the energy level diagram to the right, where g = degeneracy. What is the average value of the quantum number n, i.e., $\overline{n}$, as a function of T?

$$n = 1 \quad \underline{\qquad} \quad g = 5 \quad \text{energy} = \mathcal{E}$$

$$n = 0 \quad \underline{\qquad} \quad g = 2 \quad \text{energy} = 0$$

$$\overline{n} = \frac{\sum_i n_i \, g_i \, e^{-\overline{E}_i/kT}}{\sum_i g_i \, e^{-E_i/kT}} = \frac{0 \cdot 2 e^{-0/kT} + 1 \cdot 5 e^{-\mathcal{E}/kT}}{2 + 5 e^{-\mathcal{E}/kT}}$$

$$\overline{n} = \frac{5 e^{-\mathcal{E}/kT}}{2 + 5 e^{-\mathcal{E}/kT}}$$

(4) (20 pts)

Show that the function $-\sum\limits_{j=1}^{N} P_j \ln P_j$ subject to the constraint $\sum\limits_{j=1}^{N} P_j = 1$ is a maximum when P_J equals a constant. You do not need to determine the constant, but show all work.

Lagrange undetermined multipliers (as on homework)

minimize $f - \lambda g$

$$f = -\sum_{j=1}^{N} P_j \ln P_j \qquad g = \sum_{j=1}^{N} P_j - 1$$

so $f - \lambda g = -\sum\limits_{j=1}^{N} P_j \ln P_j - \sum\limits_{j=1}^{N} (\lambda P_j - \lambda)$

for arbitrary k:

$$\frac{d}{dP_k}(f - \lambda g) = 0 = -P_k \cdot \frac{1}{P_k} - \ln P_k - \lambda$$

$$0 = -\ln P_k - \lambda - 1$$

or $\ln P_k = -(\lambda + 1)$

$$P_k = e^{-(\lambda + 1)} \qquad \checkmark$$

λ is a constant by def.

(5) (20 pts)

Consider the $^{35}Cl_2$ molecule in its $^1\Sigma_g^+$ ground electronic state, where ^{35}Cl has a nuclear spin of 3/2.

    (a) Determine the possible nuclear spin states of the ground electronic state of $^{35}Cl_2$ and give the

    complete form of the rotational-nuclear partition function, $q_{rot\text{-}nuc}$, in terms of hB, J, k, and T.

$$I = \frac{3}{2} \text{ (fermion)} \qquad \text{so} \quad \underline{P_{total} = -1}$$

$$^1\Sigma_g^+ , \text{ so } \underline{P_{elec} = +1}$$

$$T = 3, 2, 1, 0 \qquad g_N = 2T+1 = 7, 5, 3, 1$$

$$P_{nuc} = +, -, +, -$$

$$\therefore P_{rot} = \underset{odd}{-}, \underset{even}{+}, \underset{odd}{-}, \underset{even}{+}$$

even J
odd J

$$q_{rot\text{-}nuc} = 10 \sum_{J odd} (2J+1)e^{-hBJ(J+1)/kT} + 6 \sum_{J even} (2J+1)e^{-hBJ(J+1)/kT}$$

    (b) At 300 K, what is the ratio of populations in $J=6$ and $J=5$? The rotational constant of $^{35}Cl_2$ is

    0.2439 cm^{-1}. Semi-quantitatively, how will this differ for the $^{35}Cl^{37}Cl$ case?

$$\frac{J=6}{J=5} = \frac{6(2\cdot6+1)e^{-hB6(6+1)/kT}}{10(2\cdot5+1)e^{-hB5(5+1)/kT}}$$

$$= \frac{78 e^{-42hB/kT}}{110 e^{-30hB/kT}} = \frac{78 e^{-42(0.2439)/(0.6952)(300)}}{110 e^{-30(0.2439)/(0.6952)(300)}}$$

$$= 0.699$$

for $^{35}Cl^{37}Cl$, nuclear spin statistics don't factor in, so

$$ratio = 0.699 \times \frac{110}{78} = 0.986$$

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(6) (20 pts)

Within the harmonic oscillator approximation, <u>show</u> that

(a) the molecular partition function for the vibrations of a diatomic molecule is given by $q = \dfrac{e^{-\frac{h\nu}{2k_B T}}}{1 - e^{-\frac{h\nu}{k_B T}}}$

$$q_{vib} = \sum_{n=0}^{\infty} e^{-h\nu(n+1/2)/kT} = e^{-h\nu/2kT} \sum_{n=0}^{\infty} e^{-nh\nu/kT}$$

from back page, $\quad \sum_{n=0}^{\infty} x^n = \dfrac{1}{1-x} \qquad x = e^{-h\nu/kT}$

so $\quad q = e^{-h\nu/2kT} \cdot \dfrac{1}{1 - e^{-h\nu/kT}} \qquad \checkmark$

(b) the fraction in a given vibrational state n is equal to $e^{-\frac{nh\nu}{k_B T}}\left(1 - e^{-\frac{h\nu}{k_B T}}\right)$

$$\Pi_n = \dfrac{e^{-h\nu(n+1/2)kT}}{q} = \dfrac{e^{-h\nu/2kT}\, e^{-h\nu n/kT}}{\dfrac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}}} \qquad \leftarrow \text{from (a)}$$

$$= e^{-nh\nu/kT}\left(1 - e^{-h\nu/kT}\right) \qquad \checkmark$$

(c) the fraction in <u>all</u> excited vibrational states $(n > 0)$ is simply equal to $e^{-\frac{h\nu}{k_B T}}$.

$$\Pi_{n>0} = 1 - \Pi_0 = 1 - e^{0}\left(1 - e^{-h\nu/kT}\right)$$

$$= e^{-h\nu/kT} \qquad \checkmark$$

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Miscellaneous Information

$k = 1.381 \times 10^{-23}$ J/K $= 0.6952$ cm^{-1}/K

$N_A = 6.022 \times 10^{23}$ mol^{-1}

$h = 6.626 \times 10^{-34}$ J s

$c = 2.9979 \times 10^{10}$ cm/s

1 atm $= 101,325$ Pa $= 1.01325$ bar

$\ln N! = N \ln N - N$

$$U = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{V,N}$$

$$q = \left(\frac{2\pi MkT}{h^2} \right)^{3/2} V \left(\frac{kT}{\sigma hB} \right) \left(\frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}} \right) \left(g_{e1} e^{D_e/kT} \right)$$

$$\sum_{n=1}^{\infty} x^n = \frac{1}{1-x} \quad \text{for} \ \ x < 1$$

$$\Theta_r = \frac{hB}{k} = \frac{hc\tilde{B}}{k} \qquad\qquad \Theta_V = \frac{hc\tilde{\nu}}{k}$$

$dU = TdS - pdV + \mu dN$

$A = U - TS$