Chem 534: First Exam (100 points total)

Tues, October 13, 2015

Please budget your time carefully and show all work. 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 $Q = \frac{q^N}{N!}$? Be specific about the requirements for both the numerator and denominator.

The particles are independent and identical, which leads to division by $N!$. This latter factor is valid under quantum mechanically dilute conditions, i.e., $\# q$ 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 $\mu$?

\[ Q = \frac{q^N}{N!}, \quad A = -kT \ln Q \]

since $A = U - TS$, \[ dA = -SdT - pdV + \mu dN \]

so \[ \mu = \left( \frac{\partial A}{\partial N} \right)_{TV} = -kT \left( \frac{\partial \ln Q}{\partial N} \right)_{TV} \]

\[ \ln Q = N \ln q - \ln N! = N \ln q - N \ln N + N \quad \text{(Stirling's approx)} \]

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

Since $q \gg N$ in Boltzmann limit, $\mu$ is large and negative!
(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 \( kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{V,N} \).

\[
Q = \sum_x e^{-E_x / kT} \\
\left( \frac{\partial \ln Q}{\partial T} \right)_{V,N} = \frac{1}{Q} \left( \frac{\partial Q}{\partial T} \right)_{V,N} \\
= \frac{1}{Q} \left[ \sum_x \frac{1}{kT^2} E_x e^{-E_x / kT} \right] \\
= \frac{1}{kT^2} \sum_x E_x e^{-E_x / kT} \\
= \frac{\bar{E}_x}{kT^2}
\]

(3) (10 pts)
A particular system has the energy level diagram to the right, where \( g = \text{degeneracy} \). What is the average value of the quantum number \( n \), i.e., \( \bar{n} \), as a function of \( T \)?

\[
\bar{n} = \frac{\sum n_x g_x e^{-E_x / kT}}{\sum g_x e^{-E_x / kT}} \\
\bar{n} = \frac{0 \cdot 2 e^{-0 / kT} + 1 \cdot 5 e^{-E_1 / kT}}{2 + 5 e^{-E_1 / kT}} \\
= \frac{5 e^{-E_1 / kT}}{2 + 5 e^{-E_1 / kT}}
\]

\( n = 1 \quad g = 5 \quad \text{energy} = \varepsilon \)
\( n = 0 \quad g = 2 \quad \text{energy} = 0 \)
(4) (20 pts)

Show that the function \(-\sum_{j=1}^{N} p_j \ln p_j\) subject to the constraint \(\sum_{j=1}^{N} p_j = 1\) is a maximum when \(p_j\) equals a constant. You do not need to determine the constant, but show all work.

**Lagrange undetermined multiplier (as on homework)**

minimize \(f - \lambda g\)

\[ f = -\sum_{j=1}^{N} p_j \ln p_j \quad g = \sum_{j=1}^{N} p_j - 1 \]

so \(f - \lambda g = -\sum_{j=1}^{N} p_j \ln p_j - \sum_{j=1}^{N} (\lambda p_j - \lambda)\)

for arbitrary \(\lambda\):

\[ \frac{\partial}{\partial p_k} (f - \lambda g) = 0 = -p_k \cdot \frac{1}{p_k} - \ln p_k - \lambda \]

\[ 0 = -\ln p_k - \lambda - 1 \]

\[ \ln p_k = -(\lambda + 1) \]

\[ p_k = e^{-(\lambda + 1)} \]

\(\lambda\) is a constant by def.
Consider the $^{35}\text{Cl}_2$ molecule in its $^1\Sigma_g^+$ ground electronic state, where $^{35}\text{Cl}$ has a nuclear spin of $3/2$.

(a) Determine the possible nuclear spin states of the ground electronic state of $^{35}\text{Cl}_2$ and give the complete form of the rotational-nuclear partition function, $q_{\text{rot-nuc}}$, in terms of $hB$, $J$, $k$, and $T$.

\[
J = \frac{3}{2} \quad \text{(fermion)} \quad \text{so} \quad p_{\text{total}} = -1
\]
\[
\Sigma^+ = \frac{1}{2}, \quad \text{so} \quad p_{\text{elec}} = +1
\]
\[
T = 3, 2, 1, 0
\]
\[
\therefore \quad g_J = 2T+1 = 7, 5, 3, 1
\]
\[
\therefore \quad \begin{aligned}
J_{\text{rot}} &= -J, +J, -J, +J \\
& \quad \text{odd even odd even}
\end{aligned}
\]
\[
q_{\text{rot-nuc}} = 10 \sum_{J, \text{odd}} (2J+1)e^{-\frac{hB(J(J+1))}{kT}} + 6 \sum_{J, \text{even}} (2J+1)e^{-\frac{hB(J(J+1))}{kT}}
\]
(b) At 300 K, what is the ratio of populations in $J=6$ and $J=5$? The rotational constant of $^{35}\text{Cl}_2$ is 0.2439 cm$^{-1}$. Semi-quantitatively, how will this differ for the $^{35}\text{Cl}^{37}\text{Cl}$ case?

\[
\begin{align*}
\frac{J=6}{J=5} &= \frac{6 (2J+1)e^{-\frac{hB(6(6+1))}{kT}}}{10 (2J+1)e^{-\frac{hB(5(5+1))}{kT}}} \\
&= \frac{78 e^{-\frac{42 hB}{kT}}}{110 e^{-\frac{30 hB}{kT}}} = \frac{78 e^{-\frac{42 (0.2439)}{0.6952 (300)}}}{110 e^{-\frac{30 (0.2439)}{0.6952 (300)}}} \\
&= 0.699
\end{align*}
\]

For $^{35}\text{Cl}^{37}\text{Cl}$, nuclear spin statistics don’t factor in, so

\[
\text{Ratio} = 0.699 \times \frac{110}{78} = 0.986
\]
(6) (20 pts)
Within the harmonic oscillator approximation, show that

(a) the molecular partition function for the vibrations of a diatomic molecule is given by

\[ q_{\text{vib}} = \sum_{n=0}^{\infty} e^{-\frac{\hbar \nu (n+\frac{1}{2})}{kT}} = e^{-\frac{\hbar \nu}{2kT}} \sum_{n=0}^{\infty} \frac{e^{-n\hbar \nu/kT}}{1 - e^{-\hbar \nu/kT}} \]

From back page, \( \sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \quad x = e^{-\hbar \nu/kT} \)

so \( q = e^{-\frac{\hbar \nu}{2kT}} \cdot \frac{1}{1-e^{-\hbar \nu/kT}} \) \( \checkmark \)

(b) the fraction in a given vibrational state \( n \) is equal to

\[ \Pi_n = e^{-\frac{\hbar \nu (n+\frac{1}{2})}{kT}} = e^{-\frac{\hbar \nu}{2kT}} e^{-\frac{n\hbar \nu}{kT}} \]

\[ = \frac{e^{-\frac{\hbar \nu}{2kT}}}{1-e^{-\frac{\hbar \nu}{kT}}} \]

\[ = e^{-\frac{\hbar \nu}{kT}} \left( 1 - e^{-\frac{\hbar \nu}{kT}} \right) \] \( \checkmark \)

(c) the fraction in all excited vibrational states \( (n > 0) \) is simply equal to

\[ \Pi_{n>0} = 1 - \Pi_0 = 1 - e^{-\frac{\hbar \nu}{kT}} \left( 1 - e^{-\frac{\hbar \nu}{kT}} \right) \]

\[ = e^{-\frac{\hbar \nu}{kT}} \] \( \checkmark \)
Miscellaneous Information

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

\[ N_A = 6.022 \times 10^{23} \text{ mol}^{-1} \]

\[ h = 6.626 \times 10^{-34} \text{ J s} \]

\[ c = 2.9979 \times 10^{10} \text{ cm/s} \]

1 atm = 101,325 Pa = 1.01325 bar

\[ \ln N! = N \ln N - N \]

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

\[ q = \left( \frac{2\pi MkT}{h^2} \right)^{3/2} V \left( \frac{kT}{\sigma hB} \right) \left( \frac{e^{-\hbar \nu/2kT}}{1 - e^{-\hbar \nu/kT}} \right) \left( e^{E_\nu/kT} \right) \]

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

\[ \Theta_r = \frac{hB}{k} = \frac{hc \bar{B}}{k} \quad \Theta_v = \frac{hc \bar{v}}{k} \]

\[ dU = TdS - pdV + \mu dN \]

\[ A = U - TS \]