Chemistry 410B **Exam 1** **Fall 2016**

NAME:

Instructions:

1. Keep this exam closed until instructed to begin.
2. **Please write your name on this page but not on any other page.**
3. Please silence any noisy electronic devices you have.
4. Attached sheet(s) provide potentially useful constants and equations. You may detach these from the exam.
5. To receive full credit for your work, please
   (a) show all your work, using only the exam papers, including the back of this sheet if necessary;
   (b) specify the correct units, if any, for your final answers;
   (c) use an appropriate number of significant digits for final numerical answers;
   (d) **stop writing and close your exam immediately when time is called.**

Other notes:

- **The first portion of the exam (problem 1) is worth 40 points.** Partial credit for these problems is not necessarily available.
- **Your 2 best scores of the 3 remaining problems will count towards the other 60 points.** Partial credit is available for these problems, so try each problem and do not erase any of your work.

1. **40 points.**

(a) Identify the following parameters as intensive (**I**) or extensive (**E**):

i. temperature

ii. entropy

iii. mass

(b) If the rotational partition function of HF at 298 K is 9.88, what is the probability of a molecule being found in the rotational ground state ($J = 0$)?

(c) A table of energies and degeneracies is given below for the lowest energy vibrational states of carbon dioxide. Calculate the partition function at 400 K using the data below. (The states are labeled for completeness, but are not needed for the solution.)

state	g	ϵ_{vib} (cm^{-1})
(0,0,0)	1	0
(0,1,0)	2	667
(0,2,0)	3	1334
(1,1,0)	2	2000

(d) What is the number of equipartition degrees of freedom in sulfur hexafluoride (SF_6)

i. when vibrations are *not* included?

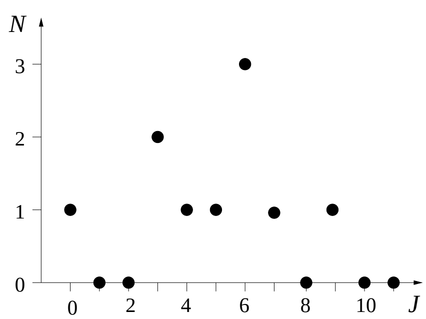
ii. when vibrations *are* included?

2. We freeze N particles into a crystal lattice, so that they are all *distinguishable*. We energize the system by means of M photons, each photon with energy ϵ_0. Each particle may absorb any number of photons. (However, the photons are *not* distinguishable; it doesn't matter in what order the photons were absorbed.)

   (a) Write an expression for the ensemble size Ω in terms of the total energy $E = M\epsilon_0$.

   (b) Find a usable expression for the entropy as a function of N and M, assuming both are large numbers.

3. The plot below shows the number of particles N in each rotational quantum level J in a simulation of ten particles. Based on these values, estimate
   (a) the Gibbs entropy of the system in SI units and
   (b) the partition function at this temperature.



4. A clever experiment measures the quantum states of neutrons bouncing on a surface in Earth's gravitational field. The potential energy of the neutrons is mgz, where the neutron mass $m = 1.675 \cdot 10^{-27}$ kg, gravitational acceleration is $g = 9.81\,\mathrm{m\,s^{-2}}$, and z is the height of the neutron (where $z \geq 0$). Use our procedure for finding the equipartition principle to find an approximate equation for the average total energy (kinetic plus potential) per neutron in this experiment as a function of the temperature. Ignore translations along x and y.

Fundamental Constants

Avogadro's number	$\mathcal{N}_A$	$6.0221367 \cdot 10^{23}$ mol^{-1}
Bohr radius	$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$	$5.29177249 \cdot 10^{-11}$ m
Boltzmann constant	k_{B}	$1.380658 \cdot 10^{-23}$ J K^{-1}
electron rest mass	m_e	$9.1093897 \cdot 10^{-31}$ kg
fundamental charge	e	$1.6021773 \cdot 10^{-19}$ C
permittivity factor	$4\pi\epsilon_0$	$1.113 \cdot 10^{-10}$ C^2 J^{-1} m^{-1}
gas constant	R	8.314510 J K^{-1} mol^{-1}
	R	0.08314510 L bar K^{-1} mol^{-1}
	R	0.08206 L atm K^{-1} mol^{-1}
hartree	$E_{\mathrm{h}} = \frac{m_e e^4}{(4\pi\epsilon_0)^2\hbar^2}$	$4.35980 \cdot 10^{-18}$ J
Planck's constant	h	$6.6260755 \cdot 10^{-34}$ J s
	$\hbar$	$1.05457266 \cdot 10^{-34}$ J s
proton rest mass	m_p	$1.6726231 \cdot 10^{-27}$ kg
neutron rest mass	m_n	$1.6749286 \cdot 10^{-27}$ kg
speed of light	c	$2.99792458 \cdot 10^{8}$ m s^{-1}

Unit Conversions

	K	cm^{-1}	kJ mol^{-1}	kcal mol^{-1}	erg	kJ
kHz =	$4.799 \cdot 10^{-8}$	$3.336 \cdot 10^{-8}$	$3.990 \cdot 10^{-10}$	$9.537 \cdot 10^{-11}$	$6.626 \cdot 10^{-24}$	$6.626 \cdot 10^{-34}$
MHz =	$4.799 \cdot 10^{-5}$	$3.336 \cdot 10^{-5}$	$3.990 \cdot 10^{-7}$	$9.537 \cdot 10^{-8}$	$6.626 \cdot 10^{-21}$	$6.626 \cdot 10^{-31}$
GHz =	$4.799 \cdot 10^{-2}$	$3.336 \cdot 10^{-2}$	$3.990 \cdot 10^{-4}$	$9.537 \cdot 10^{-5}$	$6.626 \cdot 10^{-18}$	$6.626 \cdot 10^{-28}$
K =	1	0.6950	$8.314 \cdot 10^{-3}$	$1.987 \cdot 10^{-3}$	$1.381 \cdot 10^{-16}$	$1.381 \cdot 10^{-26}$
cm^{-1} =	1.4388	1	$1.196 \cdot 10^{-2}$	$2.859 \cdot 10^{-3}$	$1.986 \cdot 10^{-16}$	$1.986 \cdot 10^{-26}$
kJ mol^{-1} =	$1.203 \cdot 10^{2}$	83.59	1	0.2390	$1.661 \cdot 10^{-14}$	$1.661 \cdot 10^{-24}$
kcal mol^{-1} =	$5.032 \cdot 10^{2}$	$3.498 \cdot 10^{2}$	4.184	1	$6.948 \cdot 10^{-14}$	$6.948 \cdot 10^{-24}$
eV =	$1.160 \cdot 10^{4}$	$8.066 \cdot 10^{3}$	96.49	23.06	$1.602 \cdot 10^{-12}$	$1.602 \cdot 10^{-22}$
hartree =	$3.158 \cdot 10^{5}$	$2.195 \cdot 10^{5}$	$2.625 \cdot 10^{3}$	$6.275 \cdot 10^{2}$	$4.360 \cdot 10^{-11}$	$4.360 \cdot 10^{-21}$
erg =	$7.243 \cdot 10^{15}$	$5.034 \cdot 10^{15}$	$6.022 \cdot 10^{13}$	$1.439 \cdot 10^{13}$	1	10^{-10}
J =	$7.243 \cdot 10^{22}$	$5.034 \cdot 10^{22}$	$6.022 \cdot 10^{20}$	$1.439 \cdot 10^{20}$	10^{7}	10^{-3}
dm^3 bar =	$7.243 \cdot 10^{24}$	$5.034 \cdot 10^{24}$	$6.022 \cdot 10^{22}$	$1.439 \cdot 10^{22}$	$1.000 \cdot 10^{9}$	0.1000
kJ =	$7.243 \cdot 10^{25}$	$5.034 \cdot 10^{25}$	$6.022 \cdot 10^{23}$	$1.439 \cdot 10^{23}$	10^{10}	1

distance	1 Å =	10^{-10} m	
mass	1 amu =	$1.66054 \cdot 10^{-27}$ kg	
energy	1 J =	1 kg m^2 s^{-2}	= 10^7 erg
force	1 N =	1 kg m s^{-2}	= 10^5 dyn
electrostatic charge	1 C =	1 A s	= $2.9979 \cdot 10^9$ esu
	1 D =	$3.3357 \cdot 10^{-30}$ C m	= $1 \cdot 10^{-18}$ esu cm
magnetic field strength	1 T =	1 kg s^{-2} A^{-1}	= 10^4 gauss
pressure	1 Pa =	1 N m^{-2}	= 1 kg m^{-1} s^{-2}
	1 bar =	10^5 Pa	= 0.98692 atm

entropy	$S_{\text{Boltzmann}} = k_{\text{B}} \ln \Omega \qquad S_{\text{Gibbs}} = -Nk_{\text{B}} \sum_i \mathcal{P}(i) \ln \mathcal{P}(i)$
temperature	$T = \left(\frac{\partial E}{\partial S}\right)_{V,N}$
canonical dist.	$\mathcal{P}(\epsilon) = \frac{g(\epsilon) e^{-\epsilon/(k_{\text{B}}T)}}{q(T)}$
Stirling's approx.	$\ln N! \approx N \ln N - N$
partition func.s	$q(T) = \sum_{\epsilon} g(\epsilon) e^{-\epsilon/(k_{\text{B}}T)}$
ideal gas	$PV = nRT$
3D box	$\varepsilon = \frac{h^2}{8mV^{2/3}}\ n^2$
	$E_{\text{vib}} = \omega_e v \qquad E_{\text{rot}} = B_v J(J+1) \qquad g_{\text{rot}} = 2J+1$
equipartition	$E = \frac{1}{2} N_{\text{ep}} N k_{\text{B}} T = \frac{1}{2} N_{\text{ep}} nRT$

Integrals

$$\int x^n dx = \frac{1}{n+1} x^{n+1} + C \qquad \int a dx = a(x + C)$$

$$\int \frac{1}{x} dx = \ln x + C \qquad \int e^x dx = e^x + C$$

$$\int \ln x dx = x \ln x - x + C \qquad \int \frac{dx}{x(a+bx)} = -\frac{1}{a} \ln\left(\frac{a+bx}{x}\right) + C$$

$$\int \sin x dx = -\cos x + C \qquad \int \cos x dx = \sin x + C$$

$$\int \sin^2(ax) dx = \frac{x}{2} - \frac{\sin(2ax)}{4a} + C \qquad \int \cos^2(ax) dx = \frac{x}{2} + \frac{\sin(2ax)}{4a} + C$$

$$\int [f(x) + g(x)] dx = \int f(x) dx + \int g(x) dx \qquad \int_a^b dx = x|_a^b = b - a$$

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}} \qquad \int_0^\infty e^{-ax^2} dx = \frac{1}{2}\left(\frac{\pi}{a}\right)^{1/2}$$

$$\int_0^\infty x e^{-ax^2} dx = \frac{1}{2a} \qquad \int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4}\left(\frac{\pi}{a^3}\right)^{1/2}$$

$$\int_0^\infty x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}} \qquad \int_0^\infty x^{2n} e^{-ax^2} dx = \frac{[1 \cdot 3 \cdot 5 \ldots (2n-1)]\sqrt{\pi}}{2^{n+1} a^{n+(1/2)}}$$