Chemistry 410B **Exam 1** **Spring 2009**

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:

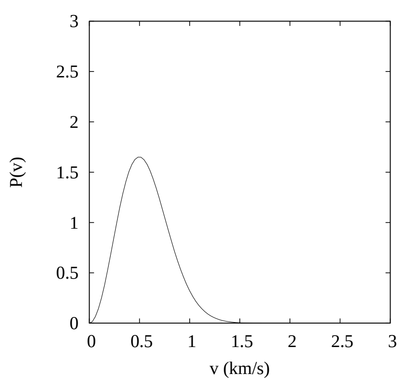
- **The first page portion of the exam is worth 40 points.** Partial credit for these problems is not necessarily available.
- **Your 2 best scores of the 3 remaining problems will count towards the other 60 points.** Partial credit is available for these problems, so try each problem and do not erase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

1. **40 points.**

   (a) Fig. 13.4 (you don't need to look at the figure) illustrates several three-dimensional box samples. The largest has 3 particles, and a degeneracy of $1.3 \cdot 10^{10}$ at an energy of $50\varepsilon_0$. What is the entropy for this sample?

   (b) Sodium dimer (Na_2) has a vibrational constant of $159.13\,\text{cm}^{-1}$. Calculate the vibrational partition function of Na_2 to three significant figures at 300.0 K.

   (c) The function $\mathcal{P}(v)$ is graphed below for a sample of Ne gas at 300 K. Sketch in the graphs of $\mathcal{P}(v)$ you would find for (a) Ar gas at 300 K, and (b) for Ne gas at 150 K. Label the new curves (a) and (b) so I can tell which is which.



   (d) How many equipartition degrees of freedom N_{ep} are present in H_2CO

      i. when vibrations are *not* included?

      ii. when vibrations *are* included?

2. The two-particle sample A has four possible states, all equally likely. Sample B, also with two particles, also has four different possible states, but the probabilities of two of the states are equal to *twice* the probabilities of the other two states; in other words, two states have probability x and two have probability $2x$. Calculate the Gibbs entropy for A and for B.

3. Write the complete integral expression that should be solved to find the fraction of molecules in a sample of helium traveling at speeds between $10^2\,\mathrm{m\,s^{-1}}$ and $10^3\,\mathrm{m\,s^{-1}}$ at $298\,\mathrm{K}$. Your final expression should include *all necessary numerical values*, simplified as much as possible. You do not need to evaluate the integral.

4. Carbonyl sulfide (OCS) has a bending mode with quantum number v_2, degeneracy $g_2 = v_2 + 1$, and a vibrational constant $\omega_2 = 520\,\mathrm{cm}^{-1}$. If 0.100% of the OCS molecules in a sample can be found in the $v_2 = 2$ vibrational level, then find the temperature T.

entropy $S_{\text{Boltzmann}} = k_B \ln \Omega \qquad S_{\text{Gibbs}} = -Nk_B \sum_i \mathcal{P}(i) \ln \mathcal{P}(i)$

3D box $\varepsilon = \frac{h^2}{8mV^{2/3}}\ n^2 \qquad g_1(\varepsilon) = \frac{32\pi V (2m^3\varepsilon)^{1/2} d\varepsilon}{h^3}$

temperature: $T = \frac{1}{k_B}\left(\frac{\partial E}{\partial \ln \Omega}\right)_{V,N}$

canonical dist. $\mathcal{P}(E) = g(E)\mathcal{P}(i) = \frac{g(E)e^{-E/(k_BT)}}{Q(T)}$

partition func.s $Q(T) = \sum_E g(E)e^{-E/(k_BT)}$

$$q_{\text{trans}}(T,V) = \left(\frac{8\pi m k_B T}{h^2}\right)^{3/2} V$$

$$Q_K(T,V) = \frac{1}{N!}\left(\frac{8\pi m k_B T}{h^2}\right)^{3N/2} V^N$$

$$\begin{aligned} Q_U(T,V) &= \left(\frac{1}{V}\right)^N \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-U(X_1,\ldots,Z_N)/(k_BT)}\ dX_1 \ldots dZ_N \\ &\equiv \left(\frac{1}{V}\right)^N Q'_U(T,V) \end{aligned}$$

$$Q_{\text{trans}}(T,V) = Q_K(T)Q_U(T,V) = \frac{1}{N!}\left(\frac{8\pi m k_B T}{h^2}\right)^{3N/2} Q'_U(T,V)$$

velocity $\mathcal{P}(\vec{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/(2k_BT)}$

Maxwell-Boltzmann $\mathcal{P}(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-mv^2/(2k_BT)}$

$$\langle v \rangle = \sqrt{\frac{8k_BT}{\pi m}}$$

$$E_{\text{vib}} = \omega_e v$$

$$E_{\text{rot}} = B_v J(J+1)$$

$$g_{\text{rot}} = 2J\ +\ 1$$

equipartition $E = \frac{1}{2} N_{\text{ep}} N k_B T = \frac{1}{2} N_{\text{ep}} n R T$

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