Chemistry 410B **Exam 1** **Spring 2012**

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) Calculate the probability of finding $^{1}H^{127}I$ in the $J = 5$ rotational state at 298 K, given that $B_e = 3.2535\,\text{cm}^{-1}$ and $q_{\text{rot}}(298\,\text{K}) = 63.7$.

(b) Write the integral necessary to calculate the number of atoms in a 1.00 mol sample of helium at 273 K that have speeds greater than $200\,\text{m}\,\text{s}^{-1}$. Include any necessary numerical values and unit conversions.

(c) Calculate the average speed of gas-phase UF_6 at 298 K.

(d) Simplify

$$\mathcal{I}(T) = 4\pi \int_0^\infty \left(e^{-u(R)/(k_B T)} - 1\right) R^2 dR$$

in the limit of the ideal gas.

2. The entropy of helium gas at 298 K and a pressure of 1.00 bar is tabulated as $126.04\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

   (a) If entropy behaves rigorously like an extensive parameter, find the entropy of a *single* He atom under these conditions.

   (b) Use the ideal gas law to determine the volume that this single atom would occupy under these conditions.

   (c) Find the number of ensemble states for the atom under these conditions.

3. Some reactions of organic molecules with iodine occur best at temperatures of up to 500 C (773 K), which just happens to be equal to $2.50\,\omega_e/k_B$. At that temperature, we may approximate the vibrational energy as a continuous function of the quantum number v. Use that approximation to estimate what fraction I_2 molecules will be in vibrational states with $v \leq 4$.

4. The disinfectant iodoform (CHI_3) has a vapor pressure of $4.5 \cdot 10^{-5}$ bar at 298 K. Assume that all the vibrational modes *except* those involving the H atom contribute to it energy according to the equipartition principle. In a sample of air at 1.00 bar and 298 K containing iodoform at its vapor pressure, estimate the fraction of the total energy that is present in the iodoform. Assume that air can be treated as a gas of diatomic molecules with no vibrational excitation at this temperature.

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: $T = \left(\frac{\partial E}{\partial S}\right)_{V,N}$

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

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

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

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

$$Q_U(T,V) = \left(\frac{1}{V}\right)^N \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-U(X_1,\ldots,Z_N)/(k_BT)}\ dX_1 \ldots dZ_N$$

$$\equiv \left(\frac{1}{V}\right)^N Q'_U(T,V)$$

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

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

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

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

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

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

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

equipartition $E = \frac{1}{2}N_{\text{ep}}Nk_BT = \frac{1}{2}N_{\text{ep}}nRT$

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	$E_\text{h} = \frac{m_e e^4}{(4\pi\epsilon_0)^2\hbar^2}$	$4.35980 \cdot 10^{-18}$ 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}	J	kJ
kHz =	$4.799 \cdot 10^{-8}$	$3.336 \cdot 10^{-8}$	$3.990 \cdot 10^{-10}$	$9.537 \cdot 10^{-11}$	$6.626 \cdot 10^{-31}$	$6.626 \cdot 10^{-34}$
MHz =	$4.799 \cdot 10^{-5}$	$3.336 \cdot 10^{-5}$	$3.990 \cdot 10^{-7}$	$9.537 \cdot 10^{-8}$	$6.626 \cdot 10^{-28}$	$6.626 \cdot 10^{-31}$
GHz =	$4.799 \cdot 10^{-2}$	$3.336 \cdot 10^{-2}$	$3.990 \cdot 10^{-4}$	$9.537 \cdot 10^{-5}$	$6.626 \cdot 10^{-25}$	$6.626 \cdot 10^{-28}$
K =	1	0.6950	$8.314 \cdot 10^{-3}$	$1.987 \cdot 10^{-3}$	$1.381 \cdot 10^{-23}$	$1.381 \cdot 10^{-26}$
cm^{-1} =	1.4388	1	$1.196 \cdot 10^{-2}$	$2.859 \cdot 10^{-3}$	$1.986 \cdot 10^{-23}$	$1.986 \cdot 10^{-26}$
kJ mol^{-1} =	$1.203 \cdot 10^{2}$	83.59	1	0.2390	$1.661 \cdot 10^{-21}$	$1.661 \cdot 10^{-24}$
kcal mol^{-1} =	$5.032 \cdot 10^{2}$	$3.498 \cdot 10^{2}$	4.184	1	$6.948 \cdot 10^{-21}$	$6.948 \cdot 10^{-24}$
eV =	$1.160 \cdot 10^{4}$	$8.066 \cdot 10^{3}$	96.49	23.06	$1.602 \cdot 10^{-19}$	$1.602 \cdot 10^{-22}$
hartree =	$3.158 \cdot 10^{5}$	$2.195 \cdot 10^{5}$	$2.625 \cdot 10^{3}$	$6.275 \cdot 10^{2}$	$4.360 \cdot 10^{-18}$	$4.360 \cdot 10^{-21}$
erg =	$7.243 \cdot 10^{15}$	$5.034 \cdot 10^{15}$	$6.022 \cdot 10^{13}$	$1.439 \cdot 10^{13}$	10^{-7}	10^{-10}
J =	$7.243 \cdot 10^{22}$	$5.034 \cdot 10^{22}$	$6.022 \cdot 10^{20}$	$1.439 \cdot 10^{20}$	1	10^{-3}
bar L =	$7.243 \cdot 10^{24}$	$5.034 \cdot 10^{24}$	$6.022 \cdot 10^{22}$	$1.439 \cdot 10^{22}$	100.0	0.1000
kJ =	$7.243 \cdot 10^{25}$	$5.034 \cdot 10^{25}$	$6.022 \cdot 10^{23}$	$1.439 \cdot 10^{23}$	10^{3}	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