Chemistry 410B **Exam 1** **Spring 2008**

NAME:

Instructions:

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

Other notes:

- **Your best scores on 4 of the 5 questions will contribute to your grade.**
- Partial credit is usually available for all problems, so try each problem and do not erase any of your work.
- Each question is worth 25 points.

1. Estimate the degeneracy of two argon atoms in a container of volume $1.00 \cdot 10^{-9}$ m^3 (one cubic millimeter) with a total energy of $2.00 \cdot 10^{-20}$ J (roughly liquid nitrogen temperature) and an energy precision of $2.5 \cdot 10^{-26}$ J (0.1 K).

2. A sample and reservoir are in contact with each other. The volumes and numbers of particles are constant for both, and the overall energy of the system is conserved. The degeneracy of the sample obeys the equation $g = AE^2$, while for the reservoir, $g_r = A_r E_r^{20}$. If the sample has an energy of 1.00 J, what is the energy of the reservoir E_r when the sample and reservoir are at the same temperature?

3. Our sample consists of N gas-phase ions of mass m at temperature T, confined in a chamber that measures from $-a/2$ to $+a/2$ along each of the X, Y, and Z axes. An electric field is applied such that the potential energy seen by each ion is $u(X, Y, Z) = \mathcal{E}_0 Z^2$, where $\mathcal{E}_0$ is a constant. The gas is sufficiently diffuse that we may neglect any potential energy for interactions between the ions.

   (a) Write an expression for the *total* potential energy of the sample, in terms of the parameters given above.

   (b) Find the *total* translational partition function of the sample, and simplify the expression as much as possible in the limit that $\mathcal{E}_0 a^2 \ll k_B T$.

4. If the vibrational partition function of an O_2 sample is 1.045, what percentage of the molecules is in the state $v = 0$?

5. Begin with a sample of 1.00 mol N_2 gas at 300 K. For each change listed in the table below, indicate the factor by which the energy E_0 of the original sample changes. Assume that the equipartition principle holds, with vibrations **not included** for temperatures below 1000 K and **included** for temperatures above 1000 K.

changing original sample by	**multiplies E_0 by factor of**
raising temperature by 300 K	
raising temperature by 900 K	
removing 0.50 mol N_2 at 300 K	
adding 3.00 mol CO_2 at 300 K	
adding 3.00 mol CO_2 and raising temperature by 900 K	

3-D box: $$\varepsilon = \frac{h^2}{8mV^{2/3}}n^2$$

$$g_1(\varepsilon) = \frac{32\pi V(2m^3\varepsilon)^{1/2}d\varepsilon}{h^3}$$

Boltzmann: $$S = k_B \ln g$$

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

canonical dist.: $$\mathcal{P}(E) = \frac{g(E)e^{-E/(k_BT)}}{Q(T)} \qquad \beta = \frac{1}{k_BT} \qquad Q(T) = \sum_E g(E)e^{-E/(k_BT)}$$

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

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

$$Q_U(\beta, V) = \left(\frac{1}{V}\right)^N \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-\beta U(X_1,\ldots,Z_N)} dX_1 \ldots dZ_N \equiv \left(\frac{1}{V}\right)^N Q'_U(\beta, V)$$

$$Q_{\text{trans}}(\beta, V) = \frac{1}{N!}\left(\frac{8\pi m}{h^2\beta}\right)^{3N/2} Q'_U(\beta, V)$$

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

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

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

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

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

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

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

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