Chemistry 410B **Exam 2** **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. The non-ideality of a gas may be expressed as a **compressibility factor**, z:

$$z \equiv \frac{PV_m}{RT}.$$

(a) Find the value of z for the ideal gas.

(b) Given the van der Waals coefficients listed below, put an X next to the name of the molecule that will have the *greatest* value of z at a pressure of 1.00 bar and 298 K. Show your reasoning or math for full credit.

molecule	a (bar L^2 mol^{-1})	b (L mol^{-1})
carbon disulfide	11.3	0.073
HCN	11.3	0.088
dichloromethane	12.4	0.087
xenon difluoride	12.4	0.070

2. Assuming the integral approximation is valid for the rotational partition function, and that the harmonic approximation is valid for vibrations, write an expression for the fraction of the sample of a gas-phase, diatomic molecule that will be in the rotational *and* vibrational ground state ($J = 0$, $v = 0$), in terms of the temperature T and the constants B and ω_e.

3. An isotopically enhanced sample has n_{DI} moles of deuterated hydrogen iodide and n_{HI} moles of common HI at 398 K. Comparison of the infrared intensities of the $v = 1 \rightarrow 2$ transition finds a ratio of 0.100 for DI molecules ($\omega_e = 1640$ cm^{-1}) in the $v = 1$ state to HI molecules ($\omega_e = 2310$ cm^{-1}) in the $v = 1$ state. What is the ratio $n_{\mathrm{DI}}/n_{\mathrm{HI}}$ in the entire sample?

4. The possible spin states for one ^{14}N nucleus, which has spin $I = 1$, are $m_I = 1$ (α), $m_I = 0$ (β), and $m_I = -1$ (γ).

   (a) We saw that the possible spin states for *two* indistinguishable $I = 1/2$ nuclei in a diatomic molecule are $\alpha\alpha$, $\alpha\beta+\beta\alpha$, $\alpha\beta-\beta\alpha$, and $\beta\beta$ (neglecting normalization). List all the distinct *two-particle* nuclear spin states for $^{14}N_2$.

   (b) Put an "**e**" next to each of these nuclear spin states that will be associated with even J rotational levels of the N_2 molecule.

5. The derivation of C_{Vm} for a fluid shows that the heat capacity is larger for a liquid than for a gas after evaluating the expression

$$C_{Vm} = \frac{3R}{2} + 2\pi\mathcal{N}_A^2 \left(\frac{\rho_m}{\mathcal{M}}\right) \int_0^\infty u(R)\, e^{-u(R)/(k_B T)} \left(\frac{u(R)}{k_B T^2}\right) R^2 dR$$

using the Lennard-Jones potential for $u(R)$. Find an equation for C_{Vm} if we instead assume the material is a solid, with a potential $u(R) = -\epsilon$ if $R_{\mathrm{LJ}} < R < 2R_{\mathrm{LJ}}$ and $u(R) = \infty$ everywhere else.

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

Some equations

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

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

partition func.s
$$q_{\rm trans}(T,V) = \left(\frac{8\pi m k_B T}{h^2}\right)^{3/2} V$$
$$Q_K(T,V) = \frac{1}{N!}\left(\frac{8\pi m k_B T}{h^2}\right)^{3N/2} V^N$$
$$Q_U(T,V) = \left(\frac{1}{V}\right)^N \int_{-\infty}^{\infty}\ldots\int_{-\infty}^{\infty} e^{-U(X_1,\ldots,Z_N)/(k_BT)}\ dX_1\ldots dZ_N$$
$$\equiv \left(\frac{1}{V}\right)^N Q'_U(T,V)$$
$$Q_{\rm trans}(T,V) = Q_K(T)Q_U(T,V) = \frac{1}{N!}\left(\frac{8\pi m k_B T}{h^2}\right)^{3N/2} Q'_U(T,V)$$
$$q_{\rm rot} \approx \frac{k_BT}{B}$$
$$q_{\rm vib} \approx \frac{1}{1\ -\ e^{-\omega_e/(k_BT)}}$$

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

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

virial
$$P = RT\left[V_m + B_2(T)V_m^2\right]$$
$$B_2(T) = -\mathcal{N}_A\frac{1}{2}\mathcal{I}(\beta) \equiv -2\pi\mathcal{N}_A\int_0^{V^{1/3}}(e^{-u(R)/(k_BT)}-1)R^2dR$$

van der Waals
$$RT = \left(P + \frac{a}{V_m^2}\right)(V_m\ -\ b)$$

Einstein equation
$$C_{Vm} = \frac{3N_A\omega_E^2 e^{\omega_E/(k_BT)}}{k_BT^2(e^{\omega_E/(k_BT)}-1)^2}$$