Chemistry 410B **Exam 2** **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) The van der Waals b coefficient for CCl_2F_2 is $0.0998\,\mathrm{L\,mol^{-1}}$. Estimate R_{LJ} in Å for this compound.

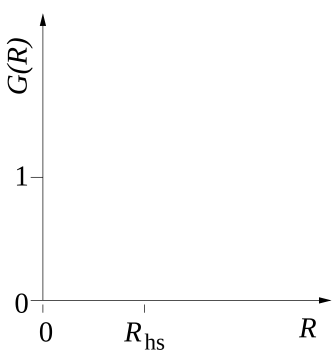
(b) Give the value of each probability for a rotating linear molecule:

i. $\lim_{T\to 0} \mathcal{P}(J=0) =$

ii. $\lim_{T\to 0} \mathcal{P}(J=4) =$

iii. $\lim_{T\to \infty} \mathcal{P}(J=4) =$

(c) Sketch the pair correlation function for a hard sphere potential, where $u(R < R_{\mathrm{hs}}) = \infty$, $u(R \geq R_{\mathrm{hs}}) = 0$.



(d) Identify each of the following particles as a fermion ("F") or boson ("B").

i. electron
ii. ^{235}U nucleus
iii. ^{235}U neutral atom
iv. $^{19}F^-$ ion
v. $^{1}H_2$ molecule

2. Calculate the pressure in bar of 1210 mol krypton in a 150.0 L container at 298 K, if $a = 2.325\,\mathrm{L^2\,mol^{-2}}$ and $b = 0.0396\,\mathrm{L\,mol^{-1}}$.

3. Find the integral approximation to the vibrational partition function for a degenerate bend in a linear molecule. The energy is $E_{\mathrm{vib}} = \omega_e v$ and the degeneracy is given by $g_{\mathrm{vib}} = v + 1$.

4. Imagine a crystal where each vibrational mode can absorb a finite amount of energy, given by the equation

$$\epsilon(T) = \frac{\epsilon_0 k_B T}{\epsilon_0 + k_B T}.$$

This expression gives the energy *per mode* in the crystal.

(a) Find an equation for C_{Vm}.

(b) Find $\lim_{T\to 0} C_{Vm}$.

(c) Find $\lim_{T\to\infty} C_{Vm}$.

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

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

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

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

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

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

$$q_{\rm rot} \approx \frac{k_B T}{B} \qquad q_{\rm vib} \approx \frac{1}{1 - e^{-\omega_e/(k_B T)}}$$

equipartition $$E = \frac{1}{2}N_{\rm ep}Nk_B T = \frac{1}{2}N_{\rm ep}nRT$$

virial/van der Waals $$P = RT\left[V_m + B_2(T)V_m^2\right] \qquad RT = \left(P + \frac{a}{V_m^2}\right)(V_m - b)$$

$$B_2(T) = -\mathcal{N}_A\frac{1}{2}\mathcal{I}(\beta) \equiv -2\pi\mathcal{N}_A\int_0^{V^{1/3}}(e^{-u(R)/(k_B T)} - 1)R^2 dR$$

$$a \approx \frac{16\pi\mathcal{N}_A^2\epsilon R_{\rm LJ}^3}{9} \qquad b \approx \frac{2\mathcal{N}_A\pi R_{\rm LJ}^3}{3}$$

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

Integrals

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

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

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

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

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

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

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

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

$$\int_0^\infty x^{2n+1}e^{-ax^2}dx = \frac{n!}{2a^{n+1}} \qquad \int_0^\infty x^{2n}e^{-ax^2}dx = \frac{[1\cdot3\cdot5\ldots(2n-1)]\sqrt{\pi}}{2^{n+1}a^{n+(1/2)}}$$

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