Chemistry 410B **Exam 3** **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) Circle the number for any statement below that is true for a perfect blackbody.

i. As T increases, more energy is radiated at low frequency.

ii. As T increases, more energy is radiated at high frequency.

iii. As T increases, the most intense radiation shifts to longer wavelength.

iv. As T increases, the number of photons *and* the average photon energy both increase.

(b) Add the periodic boundary conditions and calculate the energy in units of D for the Ising model lattice below.

$$\begin{array}{ccc} + & - & - \\ - & + & - \\ - & - & - \end{array}$$

(c) Two gas-phase samples, Ar ($\sigma = 36\,\text{Å}^2$, $m = 40\,\text{amu}$) and C_2H_2 ($\sigma = 72\,\text{Å}^2$, $m = 26\,\text{amu}$), have the same pressure and temperature. Given the values for Ar below, write the corresponding values for C_2H_2 in the same units.

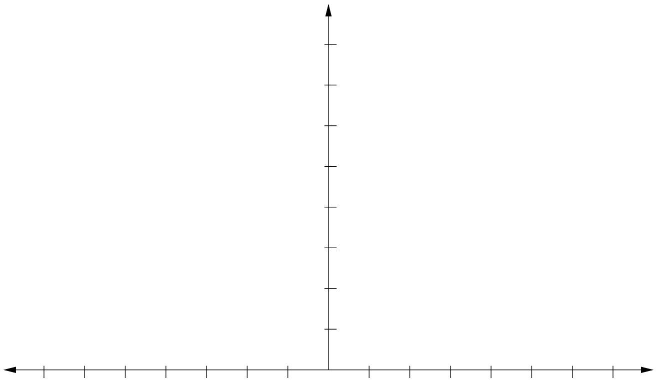
parameter	Ar	C_2H_2
$\rho\,(\mathrm{m}^{-3})$	$4.3 \cdot 10^{23}$	
$\lambda\,(\mathrm{m})$	$6.5 \cdot 10^{-6}$	
$\langle v_{\mathrm{AA}} \rangle\ (\mathrm{m\,s^{-1}})$	696	
$\gamma\,(\mathrm{s}^{-1})$	$1.1 \cdot 10^{8}$	

(d) The diffusion constant for SF_6 in air is $0.150\,\mathrm{cm^2\,s^{-1}}$ at 373 K. What is the rms distance in cm traveled by SF_6 after 1 hour?

2. In class, we graphed for 1, 2, and 3 flips of a coin the probabilities $\mathcal{P}(k)$ where

$$k = (\text{number of heads}) - (\text{number of tails}).$$

Draw the graph below for **six** coin flips, and label the axes.



3. In an ideal gas sample, PV is one measure of the energy content of the sample. If we set $PV_0 = \langle E_{\rm AB} \rangle$, find an expression for the characteristic volume V_0 in terms of only the mean free path and collision cross section.

4. The solution to the blackbody radiation problem was found by treating the energy modes of the sample as quantum harmonic oscillators. Find an equation for $\rho(\nu)$ assuming that the energy is stored in quantum **rotations** of a large number of linear molecules, each with rotational energy $\epsilon_{\text{rot}} = BJ(J+1)$ and degeneracy $g(J) = 2J+1$.

partition func.s

$$E_{\text{vib}} = \omega_e v \qquad E_{\text{rot}} = B_v J(J+1) \qquad g_{\text{rot}} = 2J+1$$

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

blackbody

$$\rho(\nu)d\nu = \frac{8\pi\nu^2 \left\langle \epsilon_{\text{vib}} \right\rangle \, d\nu}{c^3} = \frac{8\pi h \nu^3 d\nu}{c^3 (e^{h\nu/(k_B T)} - 1)}$$

collisions

$$v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}} \qquad v_P = \sqrt{\frac{2k_B T}{m}}$$

$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}} \qquad \langle v_{AA} \rangle = 4\sqrt{\frac{k_B T}{\pi m}}$$

$$\gamma = \rho\sigma \langle v_{AA} \rangle \qquad \lambda = \frac{1}{\rho\sigma}$$

random walk

$$\mathcal{P}(k) = \frac{N!}{2^N \, i! \, j!} = \frac{N!}{2^N \left(\frac{N+k}{2}\right)! \left(\frac{N-k}{2}\right)!} \approx \sqrt{\frac{2}{\pi N}} \ e^{-k^2/(2N)}$$

diffusion

$$\mathcal{P}(x) = \frac{1}{\sqrt{2\pi}\sigma} e^{-x^2/(2\sigma^2)}$$

$$\mathcal{P}(r) = \frac{4\pi}{\sqrt{8\pi^3}\sigma^3} e^{-r^2/(2\sigma^2)} r^2$$

$$\mathcal{P}(r,t) = \frac{\pi}{2(\pi D t)^{3/2}} e^{-r^2/(4Dt)} r^2 \qquad \sigma = \sqrt{2Dt}$$

$$\left\langle r^2 \right\rangle^{1/2} = \sqrt{6DT}$$

$$D = \frac{\lambda^2 \gamma}{2} \ = \ \frac{\langle v_{\text{AA}} \rangle}{2\rho\sigma}$$

Fick's laws

$$J(x_0) = -D \left(\frac{d\rho}{dx} \right)\bigg|_{x_0} \qquad \frac{d\rho}{dt} = D \frac{d^2\rho}{dx^2}$$

$$\begin{aligned}
\int x^n dx &= \tfrac{1}{n+1} x^{n+1} \ + \ C & \int a dx &= a(x \ + \ C) \\
\int \tfrac{1}{x} dx &= \ln x + C & \int e^x dx &= e^x \ + \ C \\
\int \ln x dx &= x \ln x \ - \ x \ + \ C & \int \tfrac{dx}{x(a+bx)} &= -\tfrac{1}{a} \ln \left(\tfrac{a+bx}{x} \right) \ + \ C \\
\int \sin x dx &= -\cos x \ + \ C & \int \cos x dx &= \sin x \ + \ C \\
\int \sin^2(ax) dx &= \tfrac{x}{2} - \tfrac{\sin(2ax)}{4a} \ + \ C & \int \cos^2(ax) dx &= \tfrac{x}{2} + \tfrac{\sin(2ax)}{4a} \ + \ C \\
\int [f(x) + g(x)] dx &= \int f(x) dx \ + \ \int g(x) dx & \int_a^b dx &= x|_a^b = b - a \\
\int_0^\infty x^n e^{-ax} dx &= \tfrac{n!}{a^{n+1}} & \int_0^\infty e^{-ax^2} dx &= \tfrac{1}{2} \left(\tfrac{\pi}{a} \right)^{1/2} \\
\int_0^\infty x e^{-ax^2} dx &= \tfrac{1}{2a} & \int_0^\infty x^2 e^{-ax^2} dx &= \tfrac{1}{4} \left(\tfrac{\pi}{a^3} \right)^{1/2} \\
\int_0^\infty x^{2n+1} e^{-ax^2} dx &= \tfrac{n!}{2a^{n+1}} & \int_0^\infty x^{2n} e^{-ax^2} dx &= \tfrac{[1 \cdot 3 \cdot 5 \ldots (2n-1)]\sqrt{\pi}}{2^{n+1} a^{n+(1/2)}}
\end{aligned}$$

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