Chemistry 410B **Exam 3** **Fall 2016**

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 portion of the exam (problem 1) 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) What is the probability of flipping a fair coin 6 times and getting heads 5 times?

(b) If the flux J is the same at all points along a channel, what is $d\rho/dt$ at any point Z_0?

(c) Identify the mechanism of heat transfer (conduction, convection, or radiation) in each of the following processes:

i. Sunlight passes through the atmosphere and warms the ground.

ii. The ground warms the air directly above it.

iii. The warm air rises, raising the temperature of the upper atmosphere.

(d) What is the value of the absorption coefficient ϵ for a molecule if a sample absorbs half of the light ($I = I_0/2$) at a pathlength of 1.00 cm and a concentration of $1.0 \cdot 10^{-5}$ mol/ L. (You don't need to convert any units, but give the units for your answer.)

2. Calculate the diffusion constant (in $\mathrm{cm^2\,s^{-1}}$) of helium in CO_2 at 73.8 bar and 304 K. The heterogeneous collision cross section σ_{AB} for helium and CO_2 is $32\,\mathrm{\AA}^2$. For the average relative speed, use the relative speed of He and CO_2 $\langle v_{\mathrm{AB}}\rangle = \sqrt{8k_{\mathrm{B}}T/(\pi\mu)}$.

3. We start with an ideal blackbody at 10,000 K, and measure its spectrum as a function of **wavelength** (instead of frequency). At this temperature, the blackbody emits light most strongly at $\lambda_{\mathrm{max}} = 510\,\mathrm{nm}$. We increase the temperature to 20,000 K and measure the changes. Write + if the listed parameter has increased, − if it has decreased, and **0** if it remains unchanged.

$\rho_{\mathrm{rad}}(510\,\mathrm{nm})$	
$\rho_{\mathrm{rad}}(1020\,\mathrm{nm})$	
λ_{max}	
ensemble size Ω	
ω_e	

4. A two-state system with ground state 1 and excited state 2 is immersed in a radiation field with density ρ_{12} at frequency ν_{12} to achieve steady state, so that $dN_1/dt = dN_2/dt = 0$. Let $N_1 + N_2 = N$ and let $g_1 = g_2$. Find the relationship between ρ_{12} (in units of A_{21}/B_{12}) and N_2/N and fill in the table below to show how the radiation density affects the fraction of the particles in the excited state.

N_2/N	$\rho_{12}(\nu_{12}) / (A_{21}/B_{12})$
0	
1/8	
1/4	
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

entropy	$S_{\text{Boltzmann}} = k_{\text{B}} \ln \Omega \qquad S_{\text{Gibbs}} = -Nk_{\text{B}} \sum_i \mathcal{P}(i) \ln \mathcal{P}(i)$
temperature	$T = \left(\frac{\partial E}{\partial S}\right)_{V,N}$
Stirling's approx.	$\ln N! \approx N \ln N - N$
canonical dist.	$\mathcal{P}(\epsilon) = \frac{g(\epsilon) e^{-\epsilon/(k_{\text{B}}T)}}{q(T)}$
Maxwell-Boltzmann	$\mathcal{P}_v(v) = 4\pi \left(\frac{m}{2\pi k_{\text{B}} T}\right)^{3/2} v^2 e^{-mv^2/(2k_{\text{B}}T)}$
partition func.s	$q(T) = \sum_{\epsilon} g(\epsilon) e^{-\epsilon/(k_{\text{B}}T)}$
	$E_{\text{vib}} = \omega_e v \qquad E_{\text{rot}} = B_v J(J+1) \qquad g_{\text{rot}} = 2J+1$
	$q_{\text{rot}} \approx \frac{k_{\text{B}}T}{B} \qquad q_{\text{vib}} \approx \frac{1}{1 - e^{-\omega_e/(k_{\text{B}}T)}}$
	$q_{\text{trans}}(T,V) = \left(\frac{8\pi m k_{\text{B}} T}{h^2}\right)^{3/2} V$
collisions	$v_{\text{rms}} = \sqrt{\frac{3k_{\text{B}}T}{m}} \qquad v_{\text{mode}} = \sqrt{\frac{2k_{\text{B}}T}{m}}$
	$\langle v \rangle = \sqrt{\frac{8k_{\text{B}}T}{\pi m}} \qquad \langle v_{AA} \rangle = 4\sqrt{\frac{k_{\text{B}}T}{\pi m}} \qquad \langle v_{AB} \rangle = \sqrt{\frac{8k_{\text{B}}T}{\pi \mu}}$
	$\gamma = \rho\sigma \langle v_{AA} \rangle \qquad \lambda = \frac{1}{\sqrt{2}\rho\sigma}$
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	$\mathcal{P}(x) = \frac{1}{\sqrt{2\pi}\sigma} e^{-x^2/(2\sigma^2)} \qquad \mathcal{P}(r,t) = \frac{\pi}{2(\pi D t)^{3/2}} e^{-r^2/(4Dt)} r^2$
	$\langle r^2 \rangle^{1/2} = \sqrt{6DT} \qquad D = \frac{\lambda^2 \gamma}{2} = \frac{\langle v_{\text{AA}} \rangle}{4\rho\sigma}$
Fick's laws	$J(Z_0) = -D \left(\frac{d\rho}{dZ}\right)\Big\vert_{Z_0} \qquad \frac{d\rho}{dt} = D \frac{d^2\rho}{dZ^2}$
blackbody	$\rho(\nu) d\nu = \frac{8\pi\nu^2 \langle \epsilon_{\text{vib}} \rangle\, d\nu}{c^3} = \frac{8\pi h \nu^3 d\nu}{c^3 (e^{h\nu/(k_{\text{B}}T)} - 1)}$
Beer-Lambert:	$A = -\log_{10}\left(\frac{I}{I_0}\right) = \varepsilon C l$
Einstein coefficients	$A_{21}/B_{21} = \frac{8h\pi\nu^3}{c^3} \qquad \frac{g_1 B_{12}}{g_2 B_{21}} = 1$