Chemistry 410B **Exam 2** **Spring 2012**

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) Find the average collision energy **in kJ mol^{-1}** of a 0.100 mol sample of an ideal gas at 0.831 bar and a volume of 4.00 L.

(b) Given the following values for the van der Waals coefficients, which one of these gases should have the lowest molar volume at 0.20 bar and 298 K?

molecule	a (L^2 bar/ mol^2)	b (L/ mol)
Fluoromethane	4.692	0.05264
Methanol	9.649	0.06702
Ethane	5.562	0.0638
Cyanogen	7.769	0.06901
Propane	8.779	0.08445
Sulfur dioxide	6.803	0.05636
Silane	4.377	0.05786

(c) The maximum emission from a blackbody at 770 K (about 500 C) is at a wavelength of about 6600 nm. What will be the wavelength for the most intense emission when we increase the temperature to 1540 K?

(d) Estimate the value of ln(1000!).

2. Let the energy and degeneracy of a particle in a two-dimensional box be given approximately by the expressions

$$\epsilon = \epsilon_0 n^2 \qquad\qquad g = g_0 n,$$

where n may be any positive integer, and ϵ_0 and g_0 are constants. Use the integral approximation to find an expression for the partition function of this system, in terms of the temperature, ϵ_0, and g_0.

3. (a) Find an exact expression in terms of N for the probability that in N flips of a coin, the result is tails every time *except once*.

   (b) Compare your result to the approximate solution

$$\mathcal{P}(k) \approx \sqrt{\frac{2}{\pi N}} e^{-k^2/(2N)}$$

   for the case $N = 10$.

4. Experiments in surface science (such as those done by Prof. Pullman's group) are normally carried out in vacuum chambers at extremely low pressures, to prevent the surface from becoming quickly contaminated by stray molecules. Estimate how low the pressure (in bar) must be if a square patch of surface 10.0 nm on a side is to suffer on average fewer than one collision per hour when the temperature is 298 K. Assume the chief contaminant is air, and that its molecules have an average speed $\langle v \rangle$ of $650\,\mathrm{m\,s^{-1}}$ and collision cross section of $37\,\text{Å}^2$. (The surface is stationary, so you should use $\langle v \rangle$ instead of $\langle v_{\mathrm{AA}} \rangle$.)

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}= 0.6950 cm^{-1}/K
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	$S_{\text{Boltzmann}} = k_{\text{B}} \ln \Omega \qquad S_{\text{Gibbs}} = -Nk_{\text{B}} \sum_i \mathcal{P}(i) \ln \mathcal{P}(i)$
partition func.s	$q(T) = \sum_{\epsilon} g(\epsilon) e^{-\epsilon/(k_{\text{B}}T)} \qquad q_{\text{rot}} \approx \frac{k_{\text{B}}T}{B} \qquad q_{\text{vib}} \approx \frac{1}{1 \ - \ e^{-\omega_e/(k_{\text{B}}T)}}$
	$q_{\text{trans}}(T,V) = q'_K q'_U = \left(\frac{2\pi m k_{\text{B}} T}{h^2}\right)^{3/2} V \quad \text{(ideal gas)}$
collisions	$v_{\text{rms}} = \sqrt{\frac{3k_{\text{B}}T}{m}} \qquad \langle v \rangle = \sqrt{\frac{8k_{\text{B}}T}{\pi m}} \qquad \langle v_{\text{AB}} \rangle = \sqrt{\frac{8k_{\text{B}}T}{\pi \mu}}$
	$\gamma = \rho\sigma \langle v_{AA} \rangle \qquad \lambda = \frac{1}{\sqrt{2}\rho\sigma} \qquad \rho = \frac{N}{V} = \frac{P\mathcal{N}_A}{RT}$
thermo derivatives	$dE = TdS - PdV + \mu_1 dn_1 + \ldots \qquad dH = TdS + VdP + \mu_1 dn_1 + \ldots$
	$dF = -SdT - PdV + \mu_1 dn_1 + \ldots \qquad dG = -SdT + VdP + \mu_1 dn_1 + \ldots$
isobaric heating:	$\Delta S = nC_{P\text{m}} \ln \left(\frac{T_f}{T_i}\right)$
isothermal exp:	$w_{\text{rev}} = -nRT \ln \left(\frac{V_2}{V_1}\right) \qquad w_{\text{irr}} = -P_{\min} \Delta V \qquad \Delta S = nR \ln \left(\frac{V_f}{V_i}\right)$
adiabatic exp:	$w_{\text{rev}} = C_V \Delta T \qquad \frac{V_2}{V_1} = \left(\frac{T_2}{T_1}\right)^{-C_{V\text{m}}/R} = \left(\frac{P_2}{P_1}\right)^{-C_{V\text{m}}/C_{P\text{m}}}$
Sackur-Tetrode:	$S_m = R \left\{ \frac{5}{2} + \ln \left[\left(\frac{2\pi m k_{\text{B}} T}{h^2}\right)^{3/2} \frac{RT}{\mathcal{N}_A P} \right] \right\}$
Clausius/Clapeyron:	$\frac{dP}{dT} = \frac{\Delta_\phi H}{T \Delta_\phi V} \qquad \ln P(\text{ bar}) = \frac{\Delta_{\text{vap}} H}{R} \left[\frac{1}{T_b} - \frac{1}{T}\right]$
Gibbs phase:	$d = k - p + 2$
Raoult's law:	$P_{\text{A}} = P^{\bullet}_{\text{A}} X_{\text{A}}$
Henry's law:	$P_{\text{B}} = k_X, X_{\text{B}} \qquad k_X = \lim_{X_{\text{B}} \to 0} \left(\frac{P_{\text{B}}}{X_{\text{B}}}\right)$
colligative props.	$\Delta T_f = -\frac{RT^{\bullet 2}_f X_{\text{B}}}{\Delta_{\text{fus}} H} \qquad \Pi = RT[\text{B}]$
reactions:	$\Delta_{\text{rxn}} G = \Delta_{\text{rxn}} G^{\circ} + RT \ln \Xi$
	$\ln K_{\text{eq}}(T) = -\frac{\Delta_{\text{rxn}} G^{\circ}}{RT} = -\frac{\Delta_{\text{rxn}} H^{\circ}}{RT} + \frac{\Delta_{\text{rxn}} S^{\circ}}{R}$
rate constants:	$k_{\text{SCT}} = p\sigma_{AB} \left(\frac{8k_{\text{B}}T}{\pi\mu}\right)^{1/2} e^{-E_a/(RT)} \mathcal{N}_A \qquad k_{\text{TST}} = \frac{k_{\text{B}}T}{Ch} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/(RT)}$