Chemistry 410B **Exam 3** **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) The diffusion constant of a lysozyme in water is $1.11 \cdot 10^{-6}\,\mathrm{cm^2\,s^{-1}}$, and the diffusion constant of propane in water at the same temperature is $1.21 \cdot 10^{-5}\,\mathrm{cm^2\,s^{-1}}$. If we let propane diffuse in water for $3.60 \cdot 10^{3}\,\mathrm{s}$ and measure the rms diffusion distance, how long would it take the lysozyme to reach the *same* rms diffusion distance?

(b) For the isobaric heating of an ideal gas, indicate whether each of the following is positive ("+"), negative ("−"), or zero ("0"):

i. ΔE

ii. q

iii. ΔP

iv. ΔT

v. ΔV

(c) Write a Maxwell relation based on taking the second derivative of E with respect to V and n.

(d) According to the Einstein equation for heat capacity, what is the numerical value of the heat capacity of a crystal of quartz at

i. 1000 K (assume the high temperature limit)

ii. 0 K.

2. The Fe(III) - ferrozine complex has an extinction coefficient or molar absorptivity of $2.8 \cdot 10^4 \, \mathrm{L\,mol^{-1}\,cm^{-1}}$.

   (a) What concentration would give an absorbance of 0.01 in a 1.0 cm pathlength cuvette?

   (b) At this concentration, what percent of the incident light is *absorbed*?

3. The heat capacity C_{Pm} for 1,2-dibromoethane gas is $96.8 \, \mathrm{J\,K^{-1}\,mol^{-1}}$ at 383 K and 1.00 bar.

   (a) As we heat the substance from 382 K to 384 K, how much heat (in $\mathrm{J\,mol^{-1}}$) is transferred into each of these three degrees of freedom?

      i. translation

      ii. rotation

      iii. vibration

   (b) Based on your results, roughly how many vibrational modes appear to be absorbing energy at this temperature?

4. Find what thermodynamic parameters are represented by X, Y, and Z in the equation

$$\kappa_S = \frac{C_V}{VT}\left(\frac{\partial T}{\partial X}\right)_Y \left(\frac{\partial T}{\partial X}\right)_Z .$$

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	$E_h = \frac{m_e e^4}{(4\pi\epsilon_0)^2\hbar^2}$	$4.35980 \cdot 10^{-18}$ 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	$q(T) = \sum_\epsilon g(\epsilon) e^{-\epsilon/(k_{\text{B}}T)} \qquad q_{\text{rot}} \approx \frac{k_{\text{B}}T}{B} \qquad q_{\text{vib}} \approx \frac{1}{1 - e^{-\omega_e/(k_{\text{B}}T)}}$
	$q_{\text{trans}}(T,V) = q'_K q'_U = \left(\frac{2\pi m k_{\text{B}} T}{h^2}\right)^{3/2} V$ (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:	$k_{\text{SCT}} = p\sigma_{AB} \left(\frac{8k_{\text{B}}T}{\pi\mu}\right)^{1/2} e^{-E_a/(RT)} \mathcal{N}_A \qquad k_{\text{TST}} = \frac{k_{\text{B}}T}{Ch} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/(RT)}$